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STUDIES ON THE TECHNICAL PROBLEMS IN THE PROCESSING OF CANNED SALMON

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CONTENTS

INTRODUCTION

In Japan, the production of canned salmon is undertaken at land canneries in northern Hokkaido and on floating canneries in Aleutian waters. Frozen salmon is also used as the raw material for the canning in land canneries in Hokkaido and Tohoku districts. The salmon industry is one of the largest fish-canning operations in Japan on the basis of export dollar value. There are five economic species of salmon which are used for the canning in Japan—Red (*Oncorhynchus nerka*), Pink (*O. gorbuscha*), Silver (*O. kisutch*), Chum (*O. keta*) and Chinook (*O. tschawytscha*). In addition to those species, *masu* (*O. masou*) is caught in northern waters around Japan, but the processing of it has never developed into an industry of economic importance, because the catch is not so abundant. The processing of the canned salmon in Japan is as follows:

The salmon caught by nets are taken to a land cannery or floating cannery in the fishing boats. Salmon are graded as they are unloaded at the cannery. After the grading, the heads, fins, tails and entrails of the fish are removed by a machine, "iron chink", or by hand work. Then the "sliming" is done; this consists of removing any remaining blood, slime, loose membrances, etc. by machine or by hand. After sliming, the dressed fish are fed into a cutting machine, where revolving knives cut them into slices of the proper size to fill 1-pound or 1/2-pound cans. The sliced flesh is filled into empty cans by a filling machine, or by hand. The filled cans are weighed, table salt is added, the tops of the cans are closed by vacuum closing machine, making the cans airtight. The cans are placed in large shallow trays, so called "coolers". Several of these "coolers" are placed in retorts for "sterilization" by steam under pressure. After the retorted cans are cooled, they are labelled and packed into cases which will hold 48 cans or 96 cans.

During the processing of the canned salmon, various troubles or technical problems have occurred in the past, but they have been solved after extensive endeavour. All the troubles which have occurred in the past and methods of preventing them are explained in a book by the present author, "Eiichi TANIKAWA: The processing of canned foods (in Japanese), *Kigensha*, Tokyo." The author has studied further the troubles and technical problems which have occurred since the publication of that book. It is the purpose of this paper to describe the results of those additional studies.

Before going further the author wishes to acknowledge with thanks the assistance rendered in this investigation through a grant in aid for developmental scientific research from the Ministry of Education and a grant from the Association of Exporters of Canned Salmon of Japan. Further the author wishes to express his thanks to Messrs. Minoru AKIBA, Terushige MOTOHIRO, Yoshio NAGASAWA, Shigeo SHOJI, and Takashi SUGIYAMA, for their cooperation in this work.

I. BACTERIOLOGICAL STUDIES ON DECOMPOSED CANNED SALMON

According to the results of bacteriological studies on decomposed canned salmon, there are two types of decomposition : (1) The cans are flat, but the contents liquefied, (2) Swelled. As the author has obtained both cans of two types, he has studied the cause of the decomposition, and has inspected the heat-resistance of the isolated bacteria from those samples of decomposed canned salmon, in order to ascertain the level of heating temperature-time in the processing adequate to prevent such decomposition. The problems of the softening of the meat of canned salmon has been studied by Fellers[1]. According to him, the cause of the decomposition may be aerobic spore-forming bacteria, such as *Bac. cereus* or *Bac. mesentericus* (*Bac. subtilis var.*). As to swelled can, Kawaguchi[2] has isolated *Bac. arborescent, Bac. coli, Bac. vacultus, Bac. vulgaris, Bac. salmoni*. As those bacteria were non-thermotolerant bacteria, he has stated that the cause of the swelling may be imperfect closing of the can.

The present author has isolated the bacteria which were the cause of the decomposition in cases of swelling. From the result of inspecting the thermotolerance of the isolated bacteria, he has considered the swelling to be due to the understerilization of the can.

1. On the liquefying bacteria in canned salmon

Four of a lot of cans which were prepared at a cannery in Nemuro city, Hokkaido, in August were decomposed to liquefaction. According to the cannery, the raw material was unloaded into the cannery about 12 hours after the catch, and stored in cold place over a night. The freshness of the raw salmon was good. The processing was done at 240°F (10 *lbs* pressure) for 80 minutes. The surface of the can was normally flat, but the contents of all the four cans disformed almost to liquefaction. The color of the content was discolored, the taste was somewhat sour, and the juice was cloudy. The amounts of volatile basic nitrogen (hereafter, called V.B. -N) and pH value of the contents of the four cans were estimated. The amounts of V.B.-N and pH values estimated are as follow : No. 1 can V.B.-N 35.8 *mg*%, pH 6.4; No. 2 can 38.5 *mg*%, 6.4; No. 3 can 25.7 *mg*%, 6.0; No. 4 can 45.2 *mg*%, 6.0. As to the condition of the closing of the can seams, Cover Hook (C.H) and Body Hook (B.H) of No. 1 can and No. 2 can were considerably smaller than those of the normal seams ; No. 3 can and No. 4 can were generally good. The form of those seams was not incorrect commercially. Those cans were incubated at 37° C for 3 weeks, but they did not show any abnormal appearance.

(1) *Isolation of bacteria*

By usual methods, bacteria were aerobically and anaerobically isolated. From No. 1 can two strains, *A*, *B*, from No. 2 can one strain, *C*, from No. 3 can two strains, *D*, *E*, from No. 4 can two strains *D*, *E* were obtained respectively. Those strains were all facultative anaerobes. In plate culture and Burri's culture the colonies formed were dark white. The aerobic growth of those bacteria was better than anaerobic.

(2) *Properties of the isolated bacteria and their relationship*

Observing the properties of the five isolated bacteria, strains *A*, *B* and *C* were bacilli and 2.2～2.9 μ in size. Strains *D* and *C* were short rod, 1.7～2.0 μ in size. Strains *B* and *C* were active motile with peritrichous flagellae. Strains *D* and *E* were also motile with peritrichous flagellae. All the strains were gram-positive. Observing the cultural and physiological properties, strains *A*, *B* and *C* were the same species and strains *D*, *E* were also the same, respectively. Finally the two species were identified. It was remarkable that those two isolated species were able to liquefy gelatine rapidly. Further they had ability to peptonize after the coagulation of milk. Those two species resembled *Bac. subtilis* (*A*, *B*, and *C* strains) and *Bac. subtilis var.* (*D*, *E* strains) respectively.

(3) *Heat-resistance of the isolated bacteria*

Before isolating bacteria, each about 5*g* portions of the decomposed meat was taken aseptically from the sample cans, and heated at 240°F (10 *lbs* pressure) for 10 minutes in an oil bath, in order to ascertain the heat-resistance. After the heating, the meat was inoculated into bouillon media, and then was tested for the presence of surviving bacteria. The results obtained are as shown in Table 1.

Table 1. Heat-resistance of the bacteria in the decomposed meat of the canned salmon

Heating at \ Sample	No. 1 can	No. 2 can	No. 3 can	No. 4 can
10 *lbs* pressure (240°F) for 10 minutes	+++	++−	+++	+++

As seen in Table 1, it is sure that there were thermotolerant bacteria in the decomposed cans. Then the heat-resistance of the pure cultures of the isolated bacteria was inspected and results are obtained as shown in Table 2.

As seen in Table 2, the bacteria which were isolated from the liquefied cans were thermotolerant. Strains *A*, *D* and *E* were strongly resistant. Among them strain *A* survived at heating of 243.7°F (12 *lbs* pressure) for 10 minutes. Strain *C* was inferior to strains *A*, *D* and *E* in the heat-resistance; it was destroyed at heating of 241.6°F (11 *lbs* pressure) for 10 minutes.

Table 2. Heat-resistance of the pure cultures of the isolated bacteria

Heating time \ Heating temp. / Strains		240°F (10 *lbs* press.)	242°F (11 *lbs* press.)	244°F (12 *lbs* press.)
10 minutes	*A*	+ + +	+ + −	+ + −
	B	+ + +	+ − −	− − −
	C	+ + −	− − −	± − −
	D	+ + −	+ + −	− − −
	E	+ − −	+ − −	+ − −
20 minutes	*A*	+ + +	+ + −	+ − −
	B	+ − −	+ − −	− − −
	C	+ − −	− − −	− − −
	D	− − −	+ − −	− − −
	E	− − −	+ − −	− − −
30 minutes	*A*	± − −	+ − −	− − −
	B	+ − −	− − −	− − −
	C	+ − −	− − −	− − −
	D	± − −	− − −	± − −
	E	+ − −	+ − −	− − −

(4) *The processing of canned salmon inoculated with pure cultures of the isolated bacteria*

In order to ascertain whether the isolated bacteria were the cause of the liquefaction type of the decomposition of the canned salmon, pure cultures of the isolated bacteria were inoculated into the content of the canned salmon. The raw salmon of which the freshness was good, was filled into 1/2-pound cans. When the top was closed, the pure culture was inoculated to the flesh and processed at 10 *lbs* pressure for 80 minutes as usual. The pure culture suspension was prepared by suspending the bacterial colonies from the agar slant to make the concentration of spores about 10^3 in 1 *cc* of the suspension. Two *cc* of the suspension was inoculated. After the processing of the inoculated cans, they are incubated at 37°C for two weeks. After the incubation, the condi-

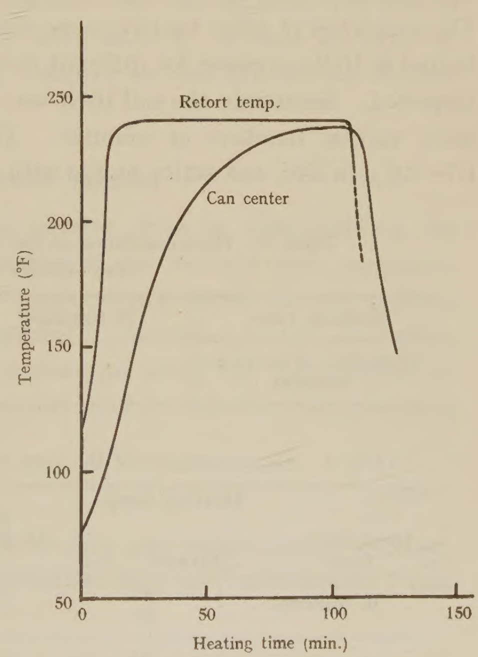


Fig. 1. Heat-penetrating curve in the processing of canned salmon (1/2-pound flat can) at 240°F (10 *lbs* pressure) for 90 minutes

tion of the contents was inspected, and the surviving bacteria were isolated again. The content of the cans inoculated with strains *A*, *B* and *E* liquefied the meat completely; the inoculated bacteria were isolated again, respectively. That is to say, the strains *A*, *B* and *E* were the bacteria which caused liquefaction of the content of the canned salmon. In the processing of the canned salmon in the retort at 240°F (10 *lbs* pressure), the heating curves were measured by a thermocouple as shown in Fig. 1. As seen in Fig. 1, when the canned salmon is sterilized in a retort, the retort temperature ascends rapidly, but the temperature of the center of cans ascends later than the retort temperature. Also, the time during which the temperature of the center of the can is maintained at near of that of the retort is less than 10 minutes within the sterilization process. So if the thermotolerant bacteria are present in the center of the can, they will survive even after the sterilization. From the results obtained, the processing at 10 *lbs* pressure for 80 minutes was understerilization.

(5) *Origin of the bacteria causing the liquefaction*

In order to know the origin of the bacteria causing the liquefaction, the thermotolerant bacteria were isolated from the soil around the cannery in which sample cans were prepared. Because it has been said that thermotolerant bacteria are sometimes isolated from the various kinds of soil. Two strains, *As* and *Bs* were obtained. The properties of those bacteria were observed and pure cultures of the bacteria were heated at 10 *lbs* pressure for different numbers of minutes, and the heat-resistance was inspected. Separately the soil itself was also heated at the same temperature for the same various numbers of minutes. The isolated strains *As* and *Bs* were bacilli, 1.7~2.0 μ in size, and active motile with peritrichous flagellae. The properties of those

Table 3. Heat-resistance of the bacteria isolated from the soil around the cannery at 10 *lbs* pressure

Heating time	10 minutes	20 minutes	30 minutes
Existence of survived bacteria	+ − −	− − −	− − −

Table 4. Heat-resistance of the pure cultures of the bacteria isolated from the soil

Heating time \ Heating temp.	Strains	240°F (10 *lbs* press.)	242°F (11 *lbs* press.)	244°F (12 *lbs* press.)
10 minutes	*As*	+ + +	+ − −	− − −
	Bs	+ + −	+ − −	− − −
20 minutes	*As*	+ + +	+ − −	− − −
	Bs	+ + +	+ − −	− − −
30 minutes	*As*	+ + −	+ − −	− − −
	Bs	+ + −	− − −	− − −

bacteria were considered to resemble those of strain *E* which were isolated from the liquefied canned salmon. The heat-resistance of the bacteria in soil and of the pure cultures of the bacteria isolated from the soil, is shown as in Tables 3 and 4. As seen in Tables 3 and 4, the bacteria isolated from the soil were also thermotolerant. Strains *As* and *Bs* were not destroyed by the heating at 10 *lbs* pressure for 10 minutes. Those strains were thermotolerant as well as the bacteria isolated from the liquefied cans. The bacteria causing the liquefaction perhaps may have originate from the soil.

(6) *Consideration*

From the experiments above described, the isolated bacteria from the liquefied content of the canned salmon were spore-forming bacteria and thermotolerant, and able to liquefy gelatine rapidly. According to the Bergey's Manual of Determinative Bacteriology[3], strains *A*, *B* and *C* were like *Bac. subtilis* and strains *D*, *E* were like *Bac. megatherium De Bary*. Those strains in cultural properties and heat-resistance resembled the bacteria isolated from the soil. It was impossible to discover the pathways from the soil to the content of can. However, the bacteria from the soil may be one of the causes of the decomposition. That is to say, the soil bacteria became attached by some chance to the salmon flesh before it was filled into the empty can; then in spite of the processing, the bacteria survived and liquefied the salmon meat. So if the raw salmon flesh is infected by those bacteria, as those bacteria will increase with the leaving time, a proper heating temperature and time for sterilization must be considered.

2. Bacteria isolated from the swelled canned salmon

From the swelled canned salmon which is another type of decomposition the causative bacteria were isolated, and the properties of the bacteria were examined. The samples of the swelled canned salmon were prepared at a certain cannery at Monbetsu, Hokkaido. They were two cans, and swelled. According to the descriptive record attached to the samples, the cans were prepared as usual, but the freshness of the raw material, the sanitary condition of the cannery, and the defect in the processing were unknown.

(1) *Isolation of bacteria*

Bacteria were isolated from the samples aerobically and anaerobically as usual. From the two swelled cans, one strain each was obtained; they are called strains *T* and *P* respectively.

(2) *Properties of the isolated bacteria and the relationship*

Examining the properties of the isolated two strains *T* and *P*, they showed rod-form 2.7~4.6 μ in size. The length of strain *P* was considerably larger than strain *T*.

Both strains were gram-positive and motile by the peritrichous flagellae. The shape of the spores formed was ellipsoid. In the glucose agar media, both strains formed gas remarkably. In respect to the cultural and physiological properties, the two isolated bacteria were like *Bac. megatherium* according to Bergey's Manual of Determinative Bacteriology[3].

(3) *Inoculation of the bacteria isolated into the canned salmon*

In order to know whether the isolated bacteria were actually the causative bacteria of the swelled cans or not, the isolated bacteria were inoculated into cans of No. 2 flat (1/2-pound) which were prepared in the same manner as in the previous experiment. The inoculated cans were processed at 10 *lbs* pressure for 90 minutes. After the processing, the cans were left in an incubator of 37°C. After 3 days' incubation, the can inoculated with strain *P* swelled, and after 5 days', that with strain *T* did likewise.

(4) *Heat-resistance of the isolated bacteria*

The heat-resistance of the isolated bacteria was examined just as was done in the case of the liquefied decomposition. Results obtained are shown in Table 5. As seen in Table 5, strains *T* and *P* were both thermotolerant. From the heat-resistance

Table 5. Heat-resistance of the bacteria isolated from the swelled canned salmon

Heating time \ Heating temp.	Strains	240°F (10 *lbs* press.)	242°F (10 *lbs* press.)	244°F (12 *lbs* press.)
10 minutes	*T*	+ ± −	± ± −	− − −
	P	+ + +	− − −	− − −
20 minutes	*T*	+ − −	+ − −	− − −
	P	+ − −	− − −	− − −
30 minutes	*T*	+ − −	+ − −	− − −
	P	+ + −	− − −	− − −

of the isolated bacteria, the cause of the swelling of the canned salmon was considered to be the survival of the thermotolerant bacteria even after the processing of the cans. The source of the bacteria contaminated into the cans during the processing may be the raw material of salmon, the soil in the cannery or the surroundings, the surface of tools and machines, or the air in the cannery.

II. STUDIES ON BACTERIAL CONTAMINATION IN CANNERIES

In order to understand the matter of bacterial contamination in the salmon cannery, the author has tried to make inspections throughout the whole course of handl-

ing of fish bodies and tools and machines used in the canning process.

(1) Experimental method

(i) *Course of the processing of canned salmon*

The course of the processing of canned salmon at a land factory is as follows :

Raw material → Washing (in water tank) → Draining (in bamboo cage) → Fins cutter (with knife by hand on table) → Head cutter (with cutting knife by hand) → Conveyor → Dressing (splitting with knife and washing in the water)→ Washing, Draining (in bamboo cage) → Fish cutter (with ranked several rotating knives by hand) → Fish bin (in bamboo cage) → Weighing (in small trays) → Clinching → Seaming → Retorting → Cooling (in water tank) → Finished product of canned salmon

(ii) *Isolation of bacteria in the course of the processing*

The samples for the isolation of bacteria were collected at certain stages in progress of work where possibility of bacterial contamination is considered to be heavy, as follows : (1) hands of head-cutting workers, (2) head cutting knife, (3) stand of head cutter, (4) surface of the conveyor belt, (5) hands of workers in dressing fish, (6) knives of dressing-workers, (7) dressing tables, (8) bamboo cages of fish bin, (9) knives of fish cutter, (10) hands of workers who arrange dressed fish on the table of the fish cutter, (11) bucket attached to the fish cutter, (12) trays for weighing cut fish, (13) hands of workers who fill the cut fish into cans, (14) dust in empty cans, (15) dust on covers which are not yet closed, (16) dust on the floor of the cannery.

The samples were collected from areas of each 2 cm^2 of points described above. For the collection use was made of absorbent cotton sterilized in 9 *cc* of physiological salt solution in each of separate test tubes. Cotton was held in pincette when wiping was done. Each sample wiped up with the absorbent cotton was returned into its own test tube containing physiological salt solution, and was shaken. The bacteria attached to the absorbent cotton were suspended in the solution which will be called the original solution. The original solution was diluted by decimal dilution. Each 1 *cc* of diluted solution in one-hundredth or in one-thousandth from the original solution was put in small test tubes respectively, and each test tube was heated for 10 minutes at 115.2°C (10 *lbs* pressure). After the heating, the solution was inoculated into agar-agar and glucose-agar and the survived bacteria were cultivated aerobically and anaerobically; the number of survived bacteria was counted, and the bacteria were isolated.

(2) Experimental results

(i) *The degree of contamination at various places*

The results obtained are shown in Table 6. As seen in Table 6, the degree of

Table 6. The degree of bacterial contamination at various places in the salmon cannery

Places isolated	Total number of bacteria (in 1 *cc* of original solution)	Number of thermotolerant bacteria survived (10 *lbs*, 10 min.)					
		Ratio of dilution	Number of bacteria before heating	Aerobic cultivation: Number of bacteria survived (in 1 *cc* of original solution)	Aerobic cultivation: Number of strains isolated	Anaerobic cultivation: Number of bacteria survived (in 1 *cc* of original solution)	Anaerobic cultivation: Number of strains isolated
1. Hands of head-cutting workers	98.1×10^6	10^{-2}	98.1×10^4	4×10^2	1	0	0
		10^{-3}	98.1×10^3	0	0	1×10^3	1
2. Head-cutting knife	342×10^6	10^{-2}	342×10^4	0	0	0	0
		10^{-3}	342×10^3	0	0	0	0
3. Stand of head cutter	225×10^6	10^{-2}	225×10^4	3×10^2	1	1×10^2	1
		10^{-3}	225×10^3	0	0	0	0
4. Surface of conveyor belt	$1,431 \times 10^6$	10^{-2}	$1,431 \times 10^4$	0	0	0	0
		10^{-3}	$1,431 \times 10^3$	0	0	0	0
5. Hands of workers in dressing fish	$2,340 \times 10^6$	10^{-2}	$2,340 \times 10^4$	0	0	0	0
		10^{-3}	$2,340 \times 10^3$	0	0	0	0
6. Dressing knife	—	10^{-2}	—	1×10^2	1	1×10^2	1
		10^{-3}	—	0	0	0	0
7. Dressing table	$24,300 \times 10^6$	10^{-2}	$24,300 \times 10^4$	0	0	1×10^2	1
		10^{-3}	$24,300 \times 10^3$	1×10^3	1	2×10^3	2
8. Bamboo cage	$1,638 \times 10^6$	10^{-2}	$1,638 \times 10^4$	0	0	0	0
		10^{-3}	$1,638 \times 10^3$	3×10^3	1	0	0
9. Knife of fish cutter	$9,720 \times 10^6$	10^{-2}	$9,720 \times 10^4$	0	0	1×10^2	1
		10^{-3}	$9,720 \times 10^3$	0	0	0	0
10. Hands of workers who arrange dressed fish on the table of fish cutter	513×10^6	10^{-2}	513×10^4	0	0	0	0
		10^{-3}	513×10^3	0	0	0	0
11. Bucket attached to the fish cutter	9×10^6	10^{-2}	9×10^4	1×10^2	1	9×10^2	2
		10^{-3}	9×10^3	0	0	8×10^3	2
12. Trays for weighing cut fish	—	10^{-2}	—	1×10^2	1	0	0
		10^{-3}	—	0	0	0	0
13. Hands of workers who fill the cut fish into cans	—	10^{-2}	—	3×10^2	2	1×10^2	1
		10^{-3}	—	0	0	0	0
14. Dust in empty cans	—	10^{-2}	—	1×10^2	1	0	0
		10^{-3}	—	0	0	0	0
15. Dust on can-covers	—	10^{-2}	—	0	0	0	0
		10^{-3}	—	0	0	0	0
16. Dust on the floor of the cannery	—	10^{-2}	—	0	0	2×10^2	2
		10^{-3}	—	1×10^3	1	1×10^3	1

contamination per unit area is the largest in the dressing of fish, especially on the dressing table, hands of workmen, knives, etc. The contamination of those points may mainly be due to the viscous substance and the visceral substance, especially to the contents in the digestive organs. The large contamination of the dressing table, hands of workmen and knives has also been investigated by Oshima[4] in a crab cannery. The thermotolerant bacteria were found on wooden substances such as tables, fish bin cages, buckets. Those facts were suggested already by Cameron[5] *et al.* Therefore, wooden equipment must be thoroughly disinfected.

(ii) *Isolation of the thermotolerant bacteria*

The bacteria which survived heating were cultivated and pure cultures obtained of 4 strains. According to Bergey's Determinative Bacteriology, those strains resembled *Bac. cereus* (*A* strain), *Bac. subtilis* (*B* strain), *Bac. mycoides* (*C* strain) and *Bac. subtilis var.* (*Bac. mesentericus vulgatus*) (*D* strain) respectively. *Bac. subtilis* and *Bac. subtilis var.* among those isolated bacteria were also amongst those previously isolated from the liquefying decomposed canned salmon. Considering the incidence of the strains, the causative bacteria of the decomposed canned salmon may be judged to have become attached to the raw material, dressing tables, or tools, and survived in the cans even after the processing; then they caused the decomposition.

Table 7. Number of thermotolerant bacteria survived

Number of bacteria (in 1*cc*) / Heating time (min.) / Strains	10^3				10^4				10^5			
	2	6	10	14	2	6	10	14	2	6	10	14
A	1	1	0	0	5	2	0	0	22	0	0	0
	0	0	0	0	1	0	0	0	20	0	0	0
	0	0	0	0	0	0	0	0	16	0	0	0
Av.	0.3	0.3	0	0	2	0.7	0	0	19.3	0	0	0
B	100	9	2	0	672	50	9	0	4,520	126	22	0
	94	6	2	0	632	45	3	0	3,356	112	13	0
	73	5	1	0	208	30	1	0	3,164	110	11	0
Av.	89	6.7	1.7	0	504	41.7	4.3	0	3,590	116	15.3	0
C	3	0	0	0	2	0	0	0	23	1	0	0
	2	0	0	0	1	0	0	0	16	1	0	0
	0	0	0	0	1	0	0	0	16	0	0	0
Av.	1.7	0	0	0	1.3	0	0	0	18.3	0.7	0	0
D	1	0	0	0	8	2	0	0	28	2	0	0
	1	0	0	0	7	0	0	0	16	2	0	0
	0	0	0	0	3	0	0	0	10	1	0	0
Av.	0.7	0	0	0	6	0.7	0	0	18	1.7	0	0

(iii) *Heat-resistance of the isolated bacteria.*

The heat-resistance of those 4 strains isolated in the previous experiment was examined at 115.2°C (10 *lbs* pressure) in various concentrations of spores (10^3, 10^4 and 10^5). The results obtained are shown in Table 7. As seen in Table 7, strain *B* was the most thermotolerant, and survived heating at 115.2°C (10 *lbs* pressure) for 10 minutes in the concentrations of spores, 10^3 or 10^5. The other strains were destroyed at the same temperature for 6 minutes. Considering those observations, if the thermotolerant bacteria contaminate the raw material or tools, and invade into cans with fish meat, they may survive by the circumstances of the processing, for example, the heat-penetration into the canned salmon. This is possible because the heating time at the same temperature as the retort is for only about 10 minutes at the center of the canned salmon.

As to the circumstances of the processing, the freshness of the raw salmon material is considered to be an important factor. If the freshness of the raw material falls, the number of attached bacteria increases and the flesh becomes soft. Then when the meat is filled into cans, it becomes closely packed and the penetration of the heat becomes more difficult than is the case in the rigid flesh of fresh meat.

III. CHANGES OF THE CHEMICAL COMPONENTS AND THE NUMBER OF BACTERIA WHEN THE RAW FLESH OF SALMON IS LEFT

When canned salmon is manufactured, if the raw material is unfresh, it is difficult to prepare a product good quality, even if great technical skill is employed. It is not too much to say that the quality of canned fish is affected by the freshness of the raw material. Therefore, it is important to inspect the freshness of the raw material and further to know the limit of its freshness.

Haughton and Hunter[6] have observed the daily changes of raw salmon which was left after the catching. The present author has also observed the daily chemical and bacterial changes of raw salmon from the estimation of the amount of V.B.-N and the number of bacteria attached. Raw materials in various stages of freshness were processed for canned salmon respectively. From the qualities of each sample of canned salmon thus manufactured, the limit of the freshness of the raw salmon as suitable raw material for commercial canned salmon was investigated.

1. Chemical and bacterial changes at the decomposition of raw salmon

(1) *Experimental material and method*

Fresh chum salmon (*Oncorhynchus keta*) (male, about 12 hours after catching) which was in rigor mortis, was used for the sample. The salmon was washed with running tap water for removal of dirty substance attached to the surface; then the

head of the salmon was cut off and visceral substances and gill removed. The salmon body was cut into several pieces. Each piece was wrapped with parchment paper and left respectively in incubator at 25° and 35°C, and in the room (15°C). After a definite length of leaving time, each piece was estimated for pH, the amount of V.B.-N and the bacterial count. At the same time, the precipitating reaction[7)] by mercury chloride solution was employed for estimation of the freshness of the meat.

(2) *Experimental results*

Results obtained are shown in Tables 8 and 9 and in Figs. 2, 3 and 4.

Table 8 shows the chemical changes of raw salmon meat; Fig. 2 shows the variation of pH and of the amounts of V.B.-N. Table 9 shows

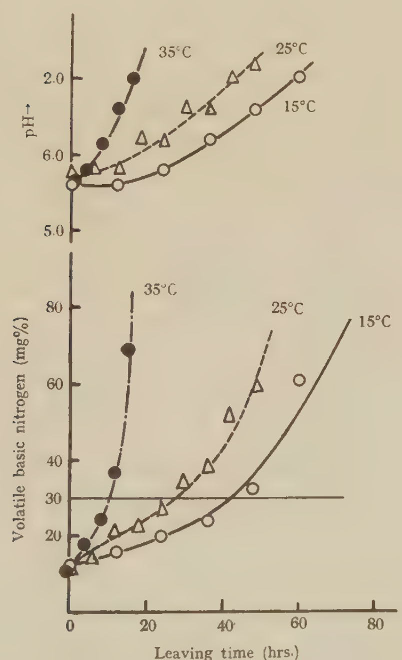


Fig. 2. Variation of pH and of the amounts of volatile basic nitrogen

Table 8. Chemical changes in the decomposition of raw salmon meat at various leaving temperatures

15°C					25°C					35°C				
Leaving time (hrs.)	V.B.-N (*mg%*)	pH	$HgCl_2$-reaction A-soln.	$HgCl_2$-reaction B-soln.	Leaving time (hrs.)	V.B.-N (*mg%*)	pH	$HgCl_2$-reaction A-soln.	$HgCl_2$-reaction B-soln.	Leaving time (hrs.)	V.B.-N (*mg%*)	pH	$HgCl_2$-reaction A-soln.	$HgCl_2$-reaction B-soln.
0	12.3	5.6	±	±	0	11.3	5.8	−	−	0	11.3	5.6	−	−
12	15.8	5.6	±	±	6	13.3	5.8	±	−	4	17.9	5.8	±	±
24	20.5	5.8	±	±	12	20.6	5.8	±	±	8	24.5	6.2	±	±
36	23.6	6.2	±	±	18	22.5	6.2	±	±	12	37.3	6.6	+	±
48	32.6	6.6	+	+	24	25.9	6.2	+	±	16	69.5	7.0	++	+
60	60.5	7.0	++	+	30	34.0	6.6	+	+					
					36	37.9	6.6	+	+					
					42	51.1	7.0	+	+					
					48	59.3	7.2	++	+					

Table 9. Bacterial changes in the decomposition of raw salmon meat at various leaving temperatures

15°C			25°C			35°C		
Leaving time (hrs.)	Total number of bacteria per *gm* of meat	Number of thermo-tolerant bacteria per *gm* of meat	Leaving time (hrs.)	Total number of bacteria per *gm* of meat	Number of thermo-tolerant bacteria per *gm* of meat	Leaving time (hrs.)	Total number of bacteria per *gm* of meat	Number of thermo-tolerant bacteria per *gm* of meat
0	2.0×10^4	5.8×10^3	0	7.5×10^4	2.8×10^3	0	2.4×10^4	3.4×10^3
12	4.2×10^4	5.2×10^3	6	4.3×10^5	3.4×10^3	4	2.2×10^5	9.3×10^3
24	7.6×10^5	8.6×10^4	12	2.9×10^6	9.0×10^4	8	1.2×10^6	4.7×10^5
36	3.4×10^6	8.4×10^5	18	2.1×10^6	1.3×10^5	12	7.2×10^6	5.4×10^5
48	4.0×10^6	1.9×10^6	24	7.4×10^6	1.4×10^6	16	1.6×10^7	1.7×10^6
60	3.0×10^6	1.8×10^6	30	8.3×10^6	4.5×10^6			
			36	5.6×10^6	6.2×10^6			
			42	1.2×10^7	5.7×10^6			
			48	1.2×10^7	7.5×10^6			

the variation of bacterial count. Fig. 3 shows the variation in total number of bacteria attached to the meat. Fig. 4 shows the variation in the number of thermotolerant bacteria which survived heating at 100°C for 30 minutes. As seen in Table 8, the amounts of V.B. -N increased in the meat which was left at 15°, 25° and 35°C,

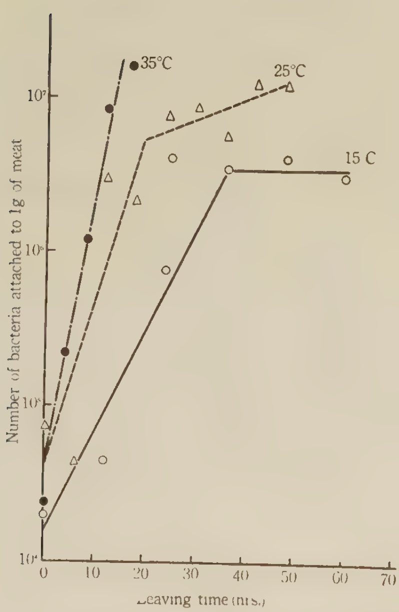


Fig. 3. Variation in the total number of bacteria attached to raw salmon meat

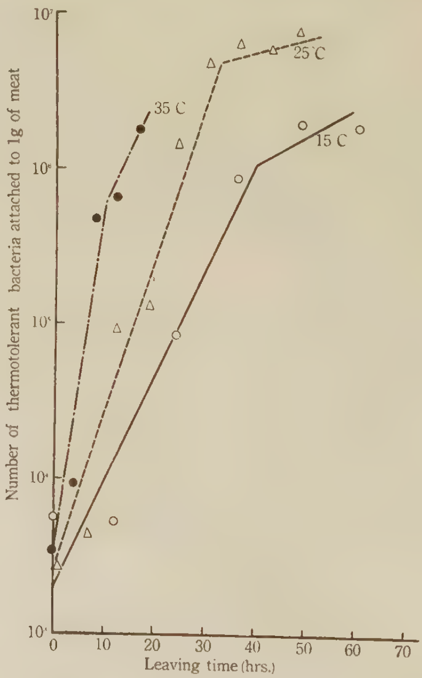


Fig. 4. Variation in the number of thermotolerant bacteria which survived heating at 100°C for 30 minutes

and the values of pH increased also; the precipitating reaction became remarkable with the lengthening of leaving time.

The increase of the pH value was independent of the advance of decomposition, so the estimation of pH is not an index of the decomposition. But the precipitating reaction can be used qualitatively for estimation of the freshness of the raw material, as the strength of the reaction is proportional to the increase of the amount of V.B. -N. When the amount of V.B.-N became more than 30 *mg*%, the precipitating reaction showed incipient putrefaction.

As seen in Table 9, the number of bacteria attached to the meat increased logarithmically at various leaving temperatures with the duration of leaving time. The degree of the increase of bacterial count was large with the rising of the leaving temperature. But the increasing of bacterial count reached to the maximum after some definite time, and then decreased. The point, at which the increasing of the total number of bacteria stopped was after 36 hours at 15°C, after 20 hours at 25°C, and after 10 hours at 35°C. In the curves of increasing of the number of thermotolerant bacteria, such a maximum point is after 40 hours at 15°C, after 33 hours at 25°C, and after 10 hours at 35°C. Comparing the increasing of total bacterial number with the increasing of the amount of V.B.-N, the point, at which the increasing of the total number of bacteria stopped, corresponded to 23.6 *mg*% of V.B.-N at 15°C, 22.5~25.9 *mg*% of V.B.-N at 25°C and 24.5 *mg*% at 35°C. Comparing the increasing of the number of the thermotolerant bacteria with increasing of the amount of V.B. -N, the same maximum point corresponded to 23.6~32.6 *mg*% at 15°C, 34.0~37.9 *mg*% at 25°C, and 37.3~69.5 *mg*% at 35°C.

From those results, it is to be noted that the point up to which the rapid increasing of the amount of V.B.-N reached after the gentle increasing of the amount of V.B.-N, was that at which the increase of the number of the bacteria became gentle. This may be due to the reason that when the bacteria grow by taking nutrition from fish meat, at the initial stage the nutrition of free state (free amino acids, etc.) is utilized by bacteria, therefore the fish meat is not yet decomposed, but at the middle stage, the autolysis of fish meat and enzymatic action of bacteria grown decompose the fish meat protein, and the lower chemical substances are yielding, so the amount of V.B.-N increases. At this stage the population of bacteria continues stable. At the point at which the amount of V.B.-N increases rapidly, the population of bacteria weakens, and the metabolism of bacteria is considered to continue.

Comparing the increasing of the total number of bacteria with that of the thermotolerant bacteria, the increasing proportion of the thermotolerant bacteria is the same as that of total number of bacteria, until the retarded growth period. But after the commencement of the retarded growth period, the increasing proportion of the thermotolerant bacteria is rather larger than that of the total number of bacteria. Almost all of the thermotolerant bacteria are in the form of spore-forming rods. Those

bacteria are not found at the initial stage of the decomposition, but with the marching of the decomposition the increasing proportion becomes larger. So in this experiment, at the initial stage of the decomposition of salmon meat, cocci or non spore-forming bacilli were found, and at the middle or final stages of the decomposition, thermotolerant bacteria were found. The point, at which the increasing of the thermotolerant bacteria stopped is more retarded than that of increasing of the total number of bacteria. The proportion of the increasing of the thermotolerant bacteria, and the heat-resistance of the bacteria will be examined in the next experiment.

2. The chemical components produced from the decomposing raw salmon meat

When the raw meat of salmon is left standing, the meat decomposes, and produces various chemical components with the increasing of the amount of V.B.-N and of the bacterial count.

(1) *Experimental method*

Samples of the raw meat of salmon were left at 15°C, and after a definite interval of leaving time, about 10 *g* of the left meat was used for the detection of chemical components produced, especially the volatile bases and volatile acids, by paper partition chromatography. For the detection of volatile bases, about 10 *g* of the left meat was put in a flask with round bottom, and 100 *cc* of dist. water and 20 *cc* of 10% NaOH solution were added to the flask. The material was steam-distilled. A receiver, in which 2~3 *cc* of 1 N HCl solution was placed, was attached to the end of the condensor. When the distillate reached to about 100 *cc*, the distillation was stopped. The distillate was evaporated on a bath, and the evaporated solution was used for the sample of chromatography. As a developer, a mixed solution of benzyl alcohol (3 volumes), glacial acetic acid (1 volume) which was saturated with water was used. Filter paper used was Toyo Filter Paper No. 50. The sample was developed in the mixed solution at 13°C (room temperature) for 8 hours by one-dimension ascending method. As spray reagent 0.1% ninhydrin buthanol solution was used. After heating, the values of Rf were calculated from the position of the spot revealed.

The paper partition chromatography for the detection of the volatile acids was carried on by Fink and Fink's method[8]. About 40 *g* of the left meat was put in a flask, 50 *cc* of dist. water and 5 *cc* of conc. H_2SO_4 soln. were put into the flask and the whole was steam-distilled. To about 200 *cc* of the distillate was added ether and ether-extraction was made at 7°C for 18 hours in a separating funnel. The volatile acids were transferred into ether layer. After the evaporation of ether, about 0.5 *cc* of brown solution was obtained. To the brown solution was added 30 *cc* of alcohol and 7.5 *cc* of conc. H_2SO_4 solution and the mixture was esterificated in an oil bath of 140°C for 24 hours. Acid which was not yet reacted by sodium corbonate was neutral-

ized and then the ester was fractionated. About 10 *cc* of ethyl ester of volatile acids was obtained. This ethyl ester was mixed with the solution which would dissolve 1.2 *g* of hydrochloride of hydroxylamine in 7.5 *cc* of methanol and the solution which would dissolve 1.4 *g* of KOH in 0.5 *cc* of methanol. After the filtration of potassium chloride, the filtrate was used as sample for the paper partition chromatography. The sample was developed with water saturated buthanol for 6 hours, and as spray reagent ferric chloride buthanol solution saturated with water was used.

(2) *Experimental results*

Results obtained are shown in Fig. 5.

In Fig. 5, the formation of volatile bases and acids is shown corresponding to the amount of V.B.-N in raw meat of salmon. As seen in Fig. 5, when the amount of V.B.-N reached to about 24 *mg*% (36 hours after leaving), cadaverine, agmatine and piperidine-like substance were found. Those bases were also found in raw salmon meat in which the amount of V.B.-N reached to about 60 *mg*%, and putrescine was newly found. At this stage, agmatine and piperidine were also surely found. With the falling of the freshness of salmon meat, the kinds of produced volatile bases increased. The mother substance of cadaverine and piperidine may be changed to piperidine via cadaverine.

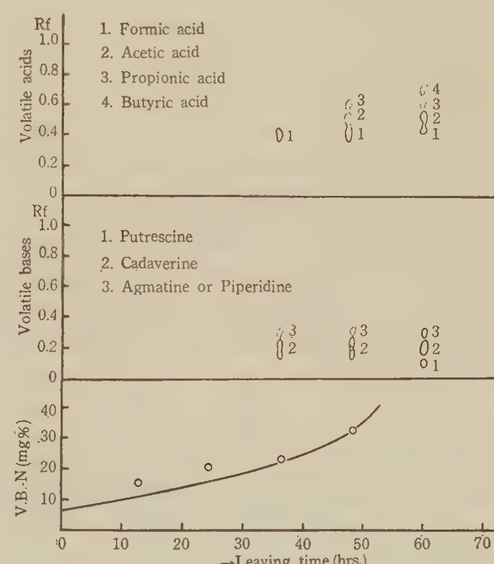


Fig. 5. The formation of volatile bases and acids at the decomposition of raw salmon meat

As to volatile acids, when the amount of V.B.-N reached about 30 *mg*% at which volatile bases began to appear, formic acid was found, and when the amount of V.B.-N reached to about 33 *mg*%, in addition to formic acid, acetic acid and propionic acid were found. When the amount of V.B.-N reached to about 60 *mg*%, at which the freshness of raw salmon meat had fallen remarkably, the presence of formic acid and acetic acid was confirmed, while propionic acid and butyric acid were found in slight quantity. With the falling of the freshness of the raw salmon meat, a series of volatile acids from formic acid to butyric acid, were found. Those facts have also been reported by Hillig and Clark[9], who have found isovalerianic acid in decomposed fish meat. The present author has not observed the formation of isovalerianic acid,

becuase the raw salmon meat used in this experiment may be not so decomposed that isovalerianic acid would appear.

As seen in the results described above, with the falling of freshness of raw salmon meat, when the amount of V.B.-N reached over about 20 *mg*%, volatile bases and acids may be formed. Therefore, as raw material of canned salmon, the fresh salmon must be used, of which the freshness is below 20 *mg*% corresponding to the amount of V.B.-N.

IV. CHANGES OF BACTERIAL FLORA DURING THE FALLING OF FRESHNESS OF SALMON MEAT AND THEIR HEAT-RESISTANCE

In the previous experiment, the author observed the variation of the total number of bacteria and number of thermotolerant bacteria attached to the raw salmon meat which was left in the room and was declining in freshness.

In the presently described experiment, the author has isolated aerobically and anaerobically the thermotolerant bacterial flora from the stale raw meat of salmon, and examined the heat-resistance of the isolated bacteria. The heat-resistance of the bacteria isolated from the raw salmon meat has been compared with that of bacteria which were often isolated from the decomposed canned salmon. The author has discussed, in this section, the limit of freshness for the raw material from the appearance of thermotolerant bacteria in the falling of the freshness of raw salmon meat.

(1) Experimental method

Fresh chum salmon (*Oncorhynchus keta*) which was made available about 12 hours after catching was subjected to head removal and dressed. The meat was left at 12°C, room temperature. After definite intervals of leaving time, in order to isolate the thermotolerant bacteria each piece of the meat was heated at 100°C for 30 minutes, and from the heated meat, bacteria were aerobically and anaerobically isolated from the plate culture.

The ratios of the appearance of the thermotolerant bacteria, aerobic or anaerobic, were calculated from each colony, of which the shapes were known previously. Then, the isolated thermotolerant bacteria were cultivated in liver-bouillon media, and were heated at 100°C for 30 minutes. After destruction of vegetative cells of the isolated bacteria by the heating, the number of spores in the liver-bouillon was calculated on Thoma's haemotometer, and adequate number of spores were suspended in 10 *cc* of physiological salt solution in test tubes. The spore-suspended solution was heated at various temperatures for different lengths of time. After the heating, the number of surviving cells was calculated on the plate culture.

(2) Experimental results

Five strains of aerobically, and 3 strains of anaerobically isolated bacteria were obtained. The anaerobically isolated bacteria were also able to grow aerobically, so the bacteria were facultative anaerobes. No obligate anaerobe was isolated. Here, after the identification of the isolated bacteria, the total number of strains isolated was known to be 5. Those 5 strains were called *SA* 1, *SA* 2, *SA* 3, *SA* 4 and *SA* 5, respectively.

SA 1 was gram-positive cocci, *SA* 2 was gram-positive rods, *SA* 3 was gram-positive rods (in chain), *SA* 4 was gram-negative rods and *SA* 5 was gram-positive short rods.

(i) *Variation of the number of thermotolerant bacteria while the salmon meat was left standing.*

The variation in number of the thermotolerant bacteria is shown in Table 10 and

Table 10. Variation of the number of thermotolerant bacteria isolated from the raw salmon meat during the leaving at 12°C

Leaving time (hrs.)	V.B.-N (*mg*%)	(a) Total number of bacteria	(b) Number of thermo-tolerant bacteria	Detecting ratio of thermotolerant bacteria isolated				
				SA 1	*SA* 2	*SA* 3	*SA* 4	*SA* 5
0 (12)	12.3	2.9×10^4	8.5×10^3	7	27	18	19	18
24 (36)	14.8	6.2×10^4	2.8×10^4	8	28	14	18	21
36 (48)	19.5	4.5×10^5	3.0×10^5	9	26	12	20	18
48 (60)	24.5	9.5×10^5	5.7×10^5	10	23	16	22	19
60 (72)	27.8	6.5×10^6	4.0×10^6	8	26	15	24	20
72 (84)	32.7	6.4×10^6	2.8×10^6	10	21	17	23	23
84 (96)	65.5	9.0×10^6	3.0×10^6	9	21	18	23	23

* Number in parenthesis shows the time after catching.

Fig. 6.

As seen in Table 10 and Fig. 6, the ratios of the number of bacteria of each strain increased or decreased with the falling of the freshness of the raw salmon meat left at room temperature.

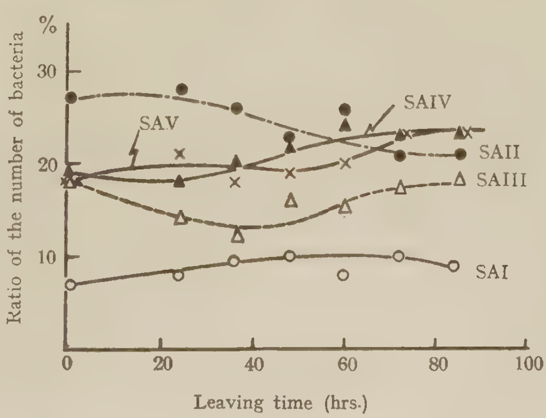


Fig. 6. Variation in the ratio of appearance of the thermotolerant bacteria isolated from the raw salmon meat

SA 1 strain was the least among 5 strains. It increased gradually and reached constancy at about 24.5 *mg*% of the amount of V.B.-N. *SA* 2 strain showed constant until about 15.8 *mg*% of the amount of V.B.-N (about 36 hours after the catching). Thereafter it decreased. *SA* 3, *SA* 4 and *SA* 5 strains were found in the same ratio during the period while the raw salmon meat was fresh. But *SA* 3 strain decreased once in the middle of falling of freshness, and increased at about 23.6 *mg*% of the amount of V.B.-N. *SA* 4 and *SA* 5 strains increased with the same tendency with the falling of the freshness. The beginning of the increase of *SA* 5 strain was later than *SA* 4 strain, and *SA* 5 strain increased at about 27.6 *mg*% of V.B.-N (at about 60 hours after the catching). *SA* 4 strain began to increase at about 15.8 *mg*% (at about 36 hours after the catching). But in the final period, both these strains showed the same ratio.

From those obtained results, if the strain of isolated bacteria of which the largest ratio of appearance is shown in each stage, takes the lead among other strains during the period of falling freshness, as Nakajima[10] said, then *SA* 2 strain took the lead and *SA* 1 strain was considered to be the next following in the

Table 11. Heat-resistance of the thermotolerant bacteria isolated from the raw salmon meat

Heating time (min.)	Heating temp. / Number of bacteria / Strains	8 *lbs* press. (112.7°C) Bacterial counts	8 *lbs* Survived ratio (%)	9 *lbs* press. (113.9°C) Bacterial counts	9 *lbs* Survived ratio (%)	10 *lbs* press. (115.2°C) Bacterial counts	10 *lbs* Survived ratio (%)	11 *lbs* press. (116.4°C) Bacterial counts	11 *lbs* Survived ratio (%)	12 *lbs* press. (117.6°C) Bacterial counts	12 *lbs* Survived ratio (%)	Spore concentration ($\times 10^4$)
10	*SA*-1	0	100	0	100	0	100	0	100	0	100	2.7
	SA-2	2.2×10^3	4.9	1.6×10^2	0.4	0	100	0	100	0	100	4.5
	SA-3	4×10^4	95	5.6×10^2	13	9.2×10^2	2	3.2×10^2	0.7	2.1×10^2	0.5	4.3
	SA-4	3.3×10^4	95	2.8×10^3	8	7.1×10^2	2	4.7×10^2	1.3	0	100	3.5
	SA-5	7.2×10^3	20	6.5×10^3	20	5.1×10^2	1.5	1.3×10^2	0.4	1.4×10^2	0.5	3.2
20	*SA*-1	0	100	0	100	0	100	0	100	0	100	2.7
	SA-2	1.6×10^2	3	0	100	0	100	0	100	0	100	4.5
	SA-3	9.3×10^3	22	2.8×10^3	6.5	4.5×10^2	1	7.6×10^2	2	2.3×10^2	0.5	4.3
	SA-4	3.3×10^4	94	2.7×10^3	7.7	2.4×10^2	0.7	1.3×10^2	0.4	0	100	3.5
	SA-5	7.1×10^3	2	5.3×10^3	1.5	4.6×10^2	1.5	1.3×10^2	0.4	1.3×10^2	0.4	3.2
30	*SA*-1	0	100	0	100	0	100	0	100	0	100	2.7
	SA-2	0	100	0	100	0	100	0	100	0	100	4.5
	SA-3	3.2×10^3	7.5	1.9×10^3	4.5	5.4×10^2	1.2	1.2×10^2	0.3	0	100	4.3
	SA-4	2.9×10^2	6.8	1.6×10^2	0.5	2.4×12^2	0.7	0	100	0	100	3.5
	SA-5	6.5×10^3	20	4.8×10^3	15	7.7×10^2	2.4	2.1×10^2	0.7	1.2×10^2	0.4	3.2

initial stage of decline of the freshness of raw salmon meat. In the middle stage of the decline, *SA* 3 strain took the lead; in final stage *SA* 3 and *SA* 5 strains took the lead. Of course, the ratio of the appearance of the strain of the isolated bacteria is not constant, but is varied according to the contamination and sanitary conditions in the cannery.

(ii) *Heat-resistance of the isolated thermotolerant bacteria*

The results of examination of heat resistance of the isolated bacteria are shown in Table 11.

As seen in Table 11, *SA* 1 strain was destroyed by heating at 112.7°C (8 *lbs* pressure) for 10 minutes. *SA* 2 strain was destroyed by heating at 113.9°C (9 *lbs* pressure) for 20 minutes. *SA* 3 strain was thermotolerant and 0.5% survived heating at 117.6°C (12 *lbs* pressure) for 20 minutes, but was destroyed at the same temperature for 30 minutes. *SA* 4 strain was destroyed by heating at 116.4°C (11 *lbs* pressure) for 20 minutes. *SA* 5 strain was the most thermotolerant, and 0.4% survived by heating at 117.6°C (12 *lbs* pressure) for 30 minutes.

Therefore, if *SA* 3, *SA* 4 or *SA* 5 strain becomes attached to the raw salmon meat, which is filled into cans, they may survive the processing at 115.2°C (10 *lbs* pressure) for 90～100 minutes, because the temperature of the center of the canned salmon is maintained for about 10 minutes at the same degree as the retort temperature. To generalize on the basis of the relation between variation of bacterial flora isolated from the raw salmon and the heat-resistance, when the raw salmon meat was left and the amount of V.B.-N reached about 20～23 *mg*%, thermotolerant bacteria, such as *SA* 3, *SA* 4 and *SA* 5 strains, began to grow. This may be due to the fact that spore forming bacteria need longer time until the germination than non-spore forming bacteria. This is important for the processing of the canned foods. That is to say, while the raw material is fresh, the ratio of appearance of the thermotolerant bacteria is small, so there is little chance of invasion into the cans.

The author has stated in the foregoing, that unless use is made of fresh raw material, of which the amount of V.B.-N is less than 20 *mg*%, canned salmon of good quality can not be obtained. This limit of freshness of raw salmon meat, 20 *mg*% of the amount of V.B.-N, will be confirmed in the next experiment. Therefore, as raw material of canned salmon the salmon meat must be fresh and non-contaminated from the bacteria which are ordinarily present in the dust or soil of the cannery, and it must be washed perfectly repeatedly with clean water during the process of the canning.

V. THE LIMIT OF FRESHNESS OF RAW SALMON MEAT AS THE SUITABLE RAW MATERIAL FOR CANNED SALMON

When the raw salmon meat is left and the freshness falls, and the amount of V.B.-N in the raw meat reaches to about 20 *mg*%, the formation of volatile bases and acids is observed and thermotolerant bacteria are found. So fresh raw salmon must be used in the preparation of canned salmon. In the present experiment, in order to confirm the belief that the limit of the freshness is about 20 *mg*% of V.B.-N in the raw material, samples of raw meat having various degrees of freshness were canned respectively by usual method, and the quality of the prepared canned salmon was inspected.

1. The limit of freshness of raw salmon meat as the raw material

(1) *Experimental method*

From fresh raw salmon (about 12 hours after catching) the head and visceral organs after splitting were removed. The dressed salmon was left at 15°C room temperature. After definite intervals of time, the cut samples of fish meat having various degrees of freshness were canned respectively and processed as usual. Three weeks after the canning, the cans were opened. When the canned salmon thus prepared was opened, the appearance, condition of the flesh, taste, odour, and the amount of V.B.-N and pH of the content were inspected.

(2) *Experimental results*

Results obtained are shown in Table 12.

Table 12. Relation between the quality of canned product and the degree of freshness of salmon meat used as raw material

Freshness of raw material (V.B.-N, *mg*%)	Results of opening inspection of canned products						
	pH of meat	V.B.-N (*mg*%)	Color of meat	Liquid	Smell	Taste	Remarks
7.2	6.8	32.1	Good	Good	Normal	Good	Edible
10.2	7.1	35.7	Ditto	Ditto	Ditto	Ditto	Ditto
15.4	7.4	43.6	Ditto	Ditto	Ditto	Ditto	Ditto
19.2	7.6	47.8	Ditto	Ditto	Ditto	Ditto	Ditto
24.5	7.8	47.2	Slightly browned	Slightly cloudy	Slightly H_2S smell	Slightly good	Question-able for eating
30.2	7.9	48.1	Browned	Cloudy	H_2S smell	No good	Not suitable for eating
36.7	7.7	48.7	Ditto	Ditto	Ditto	Ditto	Ditto
45.9	8.1	55.9	Remarkably browned	Ditto	NH_3 and H_2S smells	Ditto	Ditto

As seen in Table 12, when the raw salmon meat of which the amount of V.B.-N is about 30 *mg*%, at which point the incipient putrefaction began to be observed, is filled in the can and is processed as usual, the content is yet edible in respect to taste, but considering from the cloudiness of the liquid, the properties of floating oil on the content, the color and the taste of the content, the canned salmon meat can not be regarded as good quality. When the V.B.-N was more than 30 *mg*%, the content was not suitable for eating. But when the raw salmon meat, of which the amount of V.B.-N was less than 20 *mg*%, was filled in the can and processed as usual, the content had good quality from the various noted points of view. On the basis of those observations, the limit of the freshness of the raw salmon meat is considered to be about 20 *mg*% of the amount of V.B.-N in the raw meat.

The author has also studied the limit of the freshness for various kinds of fish as the raw material for the canned foods, and 20 *mg*% of V.B.-N was considered to be the limit.[11a-g]

2. Time required to reach the limit of the freshness of the raw salmon meat as the raw material of canned salmon

In the previous experiment, the author has stated that fresh raw salmon should be used for the raw material of the canned salmon, that is to say, within the limit of the freshness. It is convenient to know the time required to reach the limit of freshness of raw salmon meat. Of course, this time is dependent on the temperature which the material is allowed to stand. The higher the leaving temperature is, the shorter becomes the time to reach the limit. From Fig. 2(p. 79), which was obtained course of experiment III, time required to reach the limit of the freshness (20 *mg*% of V.B.-N), t_{20}, was plotted in Fig. 7 corresponding to the leaving temperature.

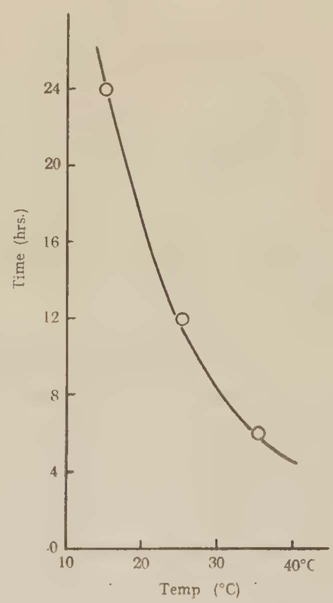


Fig. 7. Relation between the time required to reach the limit of the freshness (20 *mg*% of V.B.-N), t_{20}, and the leaving temperatures, θ°C

The relation between the leaving temperature and time required to reach the limit of the freshness is shown as equation (1).

$$\log t_\theta = \alpha - \beta\theta \quad \cdots\cdots\cdots \quad (1)$$

Here, t_θ is time required to reach the limit of the freshness of raw salmon (hrs.) corresponding to the leaving temperature (θ°C), and α and β are the constants.

If data of the curve in Fig. 7 are substituted

in equation (1) and the relation between log t_θ and temperature, θ, is plotted, *a*-line is obtained as a straight line shown in Fig. 8.

This relation is shown as equation (2).

$$\log t_\theta = 1.83 - 0.03\,\theta \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

As the time at which the raw salmon was caught and carried to the cannery is not accurately known, so about 10 hours at 15°C should be reduced to the time required experimentally to reach the limit as a safety factor from experience. Here a line containing a safety factor was drawn parallel to *a*-line in Fig. 8 and this line is called *b*-line.

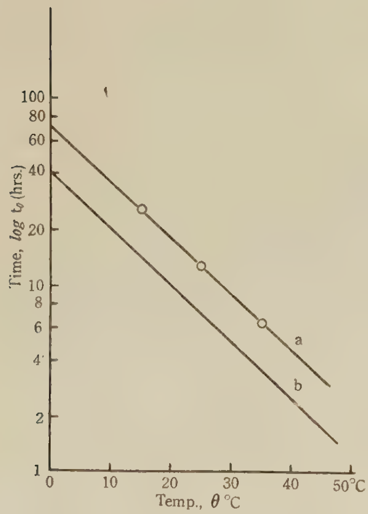


Fig. 8. Relation between the values of "log t_{20}" and leaving temperatures, θ°C

Table 13. Relation between the leaving temperature, (θ°C), and the maximum leaving time, (t_θ) of raw material

Temp. (θ°C)	Time (t_θ)
0	40 hrs.
5	28
10	20
15	14
20	9.8
25	6.8
30	4.8
35	3.4
40	2.4

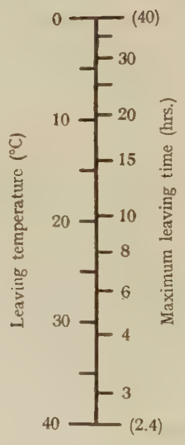


Fig. 9. Time required to reach the limit of the freshness as raw material at various leaving temperatures

The values of t_θ and θ indicated from *b*-line in Fig. 8 are shown in Table 13. The values in Table 13 are drawn in a scale diagram as shown in Fig. 9. From the scale diagram, the maximum leaving time of raw salmon at various temperatures can be known. So, when the raw salmon is carried into the cannery, if the temperature in the cannery is known by a thermometer, the leaving time permissible to the limit of freshness can be determined. If the raw salmon is processed for the canning within the maximum time, for example, at 35°C within 3.4 hours, at 25°C within 6.8 hours, at 15°C within 14 hours, canned salmon of good quality will be obtained.

The time required to reach the limit (by the present author) agrees with Haughton and Hunter's results[6] which were obtained by organoleptical tests.

VI. CALCULATION OF PROCESSING TIME AT DIFFERENT TEMPERATURES FOR VARIOUS DEGREES OF FRESHNESS OF RAW SALMON

In the processing of canned foods, it is important to determine the processing temperature and time. In order to know the equivalent processes at different temperatures, mathematical calculation of the sterilizing value of processes devised by Bigelow[12], Ball[13] and Stumbo[14] is employed. In the mathematical calculation, in the first place, the processing temperature for the kind of canned foods should be given. Then at the given processing temperature, the processing time may be calculated from the heat-penetration curve of the canned food and thermal death time curve or thermal destruction time curve of bacteria capable of spoiling the food. Then, what degree of processing temperature should be determined for various sorts of canned foods? The processing temperature should be between the lowest temperature at which bacteria can be killed, and on other hand, the highest temperature within which the normal taste, color, flavor of the content can be maintained. As to the canned salmon which has a hard backbone, the processing temperature should be that, within which the hard backbone can be softened to a degree to where it can be eaten without difficulty.

If the highest and lowest temperatures are determined, the processing time may be calculated between those two temperatures. Generally speaking, the higher the processing temperature is, the more the color of the content changes, the more burning smell is created, and the more remarkable is the change of the chemical components. For example, it is known that canned crab has a lower processing temperature (108°~110°C) than other canned fish.

As to canned salmon, Wakamatsu[15] has inspected the quality of canned salmon which was processed at 116.2°C (10 *lbs* pressure), 121°C (15 *lbs* pressure) and 126°C (20 *lbs* pressure). In the canned salmon processed at 15 *lbs* pressure and 20 *lbs* pressure, the amount of crude fat in the meat increased remarkably whilst amount of the crude protein decreased, and larger amounts of volatile bases and hydrogen sulfide are formed than in product processed at 10 *lbs* pressure. Especially the amounts of myosin-nitrogen and myogen-nitrogen decreased more remarkably in the canned salmon meat processed at 15 *lbs* or 20 *lbs* pressure than in that processed at 10 *lbs* pressure. As described below, the author has studied the relation between the processing temperature and the quality of the canned salmon meat, and observed that the highest permissible processing temperature is 117.6°C (12 *lbs* pressure) from the condition of the color, taste, flavor of the content and the amount of hydrogen sulfide formed in the meat.

Next, in order to determine the minimum reasonable processing temperature,

determination must be made of the temperature required to soften the backbone in the canned salmon and to destroy the bacteria attached to the raw salmon meat. If the number of bacteria attached to the raw salmon meat increases with the falling of the freshness of the meat, the processing time should be prolonged if processing is being done at the same temperature, at which the fresh meat is processed.

It is convenient for the technologists in canneries that considering those factors influencing the processing, the adequate processing temperature is determined; then that the processing time corresponding to the temperature is determined, and that those relations are set forth in simple scales. The author has tried to draw up such scales by studying the relation between the number of bacteria attached to the raw salmon meat and the freshness, and that between the processing temperature-time and the softening of backbone in the content. It has come to some interesting conclusions.

1. The velocity of decomposition of raw salmon meat in the initial stage

In the previous experiment, the author has observed that the limit of freshness of raw salmon meat for canned salmon is about 20 *mg*% of the amount of V.B.-N, and that when the raw salmon of which the amount of V.B.-N is more than 30 *mg*% is processed, the product is scarcely suitable for eating.

Kimata[16] has offered an equation of the decomposing velocity of fish meat, considering that the increase of the amount of V.B.-N with the falling of the freshness follows upon a monomolecular autolytic reaction. But in the curves of the formation of the amount of V.B.-N in various kinds of fish meat, the author has ascertained that the decomposing velocity of fish meat does not follow the equation of monomolecular autolytic reaction until the formation of 30 *mg*% of the amount of V.B.-N, but follows a hyperbolic equation. The raw fish meat, of which the amount of V.B.-N is more than 30*mg*%, is not suitable material for canned foods.

Here, the author has devised the following equation applied until the incipient putrefaction (in the initial stage of the decomposition).

$$V = pt^2 + V_0 \quad \cdots\cdots\cdots\cdots \quad (3)$$

Here "V" is the amount of V.B.-N in the fish meat after "t" hours, and "V_0" is the initial amount of V.B.-N in the fish meat when it is carried into the cannery; "p" is the coefficient of the decomposing velocity in the initial stage. Data of Table 8 (p. 79) which were obtained by leaving raw salmon meat at various temperatures were substituted in equation (3), and values of "p" at various temperatures were calculated. The values "p" were 0.023 at 25°C and 0.013 at 15°C.

The relation between the leaving temperature "T" and the coefficient of the decomposing velocity of raw salmon meat in the initial stage is graphed in Fig. 10.

If the values of "p" at 15°C or 25°C and values of "V_0" are substituted in equa-

tion (3) and values of V are calculated, and if the calculated values of "$V_{calc.}$" are compared with values of $V_{interp.}$ (the amount of V.B.-N after "T" hours) obtained experimentally during the leaving of raw salmon meat, the confidence of values of "$V_{interp.}$" was almost the same until 30 $mg\%$ of the amount of V.B.-N in the meat, as seen in Table 14.

That is to say, the curve of the formation of the amount of V.B.-N until 30 $mg\%$, was found to follow a quadratic equation.

However, if the leaving temperature is higher, 35°C, the curve of the formation of the amount of V.B.-N after the leaving does not follow a quadratic equation. So when the leaving temperature is higher, a quadratic equation can not be applied. For reference, values of "p" are shown for various kinds of fish in Table 15. As seen in Table 15, salmon meat is less decomposable than that of other fishes in the initial stage.

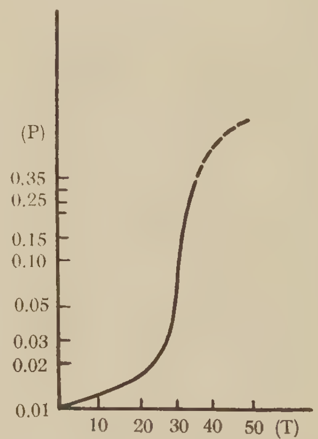


Fig. 10. Relation between the leaving temperature (T) and the coefficient of the decomposing velocity (p) of raw salmon meat in the initial stage

Table 14. Comparison on the theoretical value of "V" (volatile basic nitrogen formed) and the interpolated value of "V"

15°C (p=0.013)			25°C (p=0.023)		
t (hrs.)	$V_{calc.}$	$V_{interp.}$	t (hrs.)	$V_{calc.}$	$V_{interp.}$
0	V_0=12.3	12	0	V_0=11.3	11
12	14.2	14	6	12.1	12
24	19.8	19	12	14.6	15
36	29.1	26	18	18.8	19
48	42.3	33	24	24.5	25
60	59.1	56	30	32.0	32
			36	41.1	36
			42	51.9	48
			48	64.3	53

Table 15. p values of various kinds of fish

Fishes / Temp. (°C)	Salmon (*Oncorhynchus keta*)	Squid (*Ommastrephes sloani pacificus*)		Crab		Atka mackerel (*Pleurogrammus azonas*)	Mackerel (*Scomber japonicus*)	Saury (*Cololabis saira*)
		Summer	Autumn	*Paralithodes camtschatica*	*Erimacrus isenbeckii*			
25	0.023	0.132	0.031	0.061	0.05	0.038 (20°C)	0.170	0.032 (27°C)
15	0.013	—	—	0.035	—	—	—	0.015 (17°C)

2. Relation between the degree of falling of freshness and the leaving temperature-time of raw salmon meat

From equation (3),

$$\frac{V-V_0}{p}=t^2 \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (4)$$

is obtained, therefore,

$$\log p+2\log t=\log(V-V_0) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (5)$$

that is, equation (5) can be expressed by

$$P_{(p)}+t_{(t)}=V_{(v)} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (6)$$

The relation which is obtained by equation (6) is manifested by a monogram applying $W=U+V$. Here ,the value of $(V—V_0)$ is restricted $0 \leqq V—V_0 \leqq 30$, because the value of "V" has been restricted until 30 *mg*%. From the experimental results obtained previously concerning various kinds of fish, time "t" required to reach 30 *mg*% of the amount of V.B. -N was within 50 hours, therefore the range of "t" is $0 \leqq t \leqq 50$. The value of "p" was below 0.35 at 35°C of the leaving temperature, therefore the range of the values of "p" is considered to be $0.01 \leqq p \leqq 0.35$.

In order to make a scale showing the relation between the leaving temperature-time and the freshness of raw salmon, ratios of scales of "p", "t", and "$V—V_0$", of 10 *cm* length were calculated.

From $0 \leqq T \leqq 50$, $0 \leqq 2\log t \leqq 84.5$,
$0 \leqq m\{2\log t\} \leqq 84.5$ is obtained.

Here, if $84.5m$ is 10 (*cm*), $m=10/84.5=0.1182$ (*cm*)
that is, one unit is 0.1182 *cm*.
Then, from $0.01 \leqq p \leqq 0.35$, $0 \leqq n\log 100 \leqq 54n$
Therefore, $54n=10$, that is, $n=10/54=0.185$ (*cm*)
Therefore, scale coefficient of the scale of "$V-V_0$" is

$$\frac{mn}{m+n}=\frac{0.118\times0.185}{0.118+0.185}=\frac{0.0218}{0.303}=0.0722$$

Here, scales of "p", "t" and "$V—V_0$" are drawn as follows:
for scale of "p", $y=0.185\{\log 100p\}$
for scale of "t", $x=0.118\{2\log t\}$
for scale of "$V—V_0$", $z=0.072\{100(V—V_0)\}$
{The distance between the scale of "p" and the scale of "$V—V_0$"}:
{The distance between the scale of "$V—V_0$" and the scale of "t"}$=n:m$
$=0.185:0.118=11:16$.

The values of "x", "y", "z", are shown in Table 16 and Fig. 11.

Table 16. Scale coefficients representing the relation among the values of p, V and t

p-scale		$(V\text{-}V_0)$-scale		t-scale	
p	y	V	x	t	z
0.01	0	0.1	1.44	0	0
0.02	1.11	0.2	1.88	5	3.3
0.03	1.77	0.3	2.06	10	4.76
0.05	2.60	0.5	2.45	15	5.56
0.10	3.70	1.0	2.88	20	6.34
0.15	4.35	2.0	3.30	25	6.62
0.20					
0.25	4.82	5.0	3.88	30	7.00
0.30	5.20	7.0	4.10	35	7.28
0.35	5.49	10.0	4.32	40	7.55
	5.70	12.0	4.44	45	7.80
		15.0	4.58		
		17.0	4.66		
		20.0	4.76		
		25.0	4.80		
		30.0	4.82		

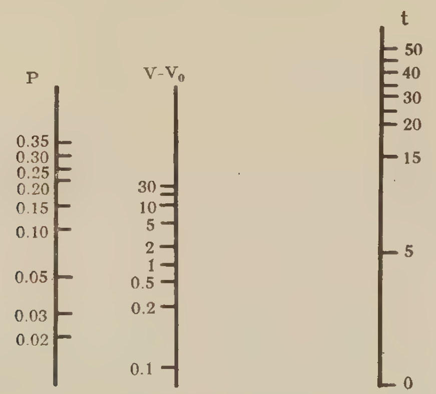


Fig. 11. A diagram showing the relation among the values of p, $V\text{-}V_0$ and t

3. Relation between the increase of the amount of V.B.-N and of the bacterial number with the falling of freshness

From Table 10 (p. 85), when the increases of bacterial count are drawn to the right side of the scale of "$V—V_0$" in Fig. 11, the relation is shown as in Fig. 12. The relation between bacterial number and the amount of V.B.-N which was observed by Tarr[17] agreed on the whole with the present author's observation.

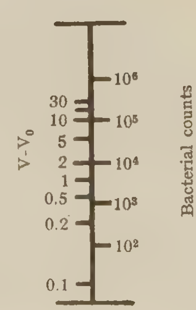


Fig. 12. A scale showing the relation between the bacterial count and the increased amount of volatile basic nitrogen

4. Relation between the leaving temperature and the bacterial count

Here, Figs. 10, 11 and 12 are together drawn as in Fig. 13. If the leaving temperature of the raw salmon in a cannery is known, cross the perpendicular line corresponding to the given temperature and the hyperbolic line showing the relation

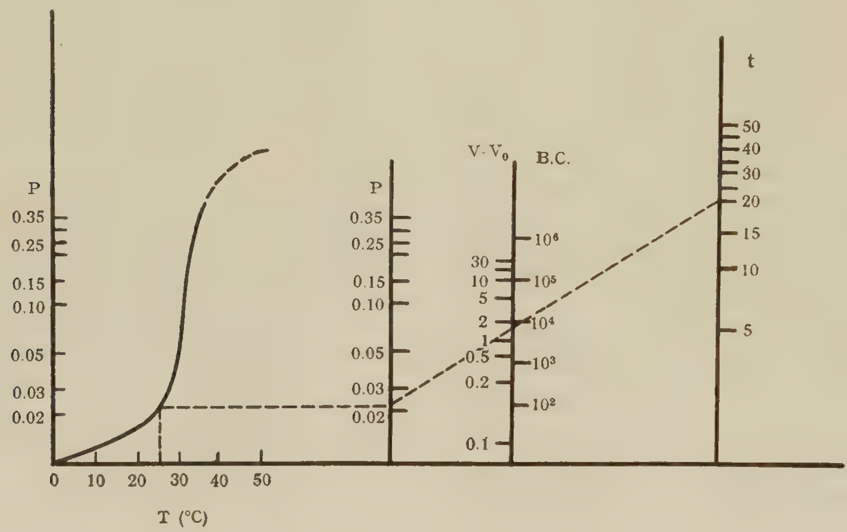


Fig. 13. A diagram showing the relation among the values of T, p, V-V_0, $B.C.$ (bacterial count) and t

between the coefficient of the decomposing velocity in the initial stage and the leaving temperature. From the point of crossing, a horizontal line is drawn and is crossed with "p"-scale. The cross point is combined with some leaving time on "t"-scale by a straight line. The point at which the straight line and "V—V_0"-scale cross, shows the increase of the amount of V.B.-N on the left side and the bacterial counts on the right side of "V—V_0"-scale.

5. Relation between the processing temperature-time and the softening of backbone in the canned salmon

The softening of the backbone by heating is owing to the gelatination of collagen which is combined with calcium and phosphrous in osseous tissue, and to the deforming of the tissue.

The backbone in canned marine foods, such as canned salmon, must be easily crushed with the teeth when they are eaten. Then, what strength of processing softens the backbone ? Even if the processing temperature is low, a longer processing time can soften the backbone. The power of softening of the backbone is concerning

with the integral multiplying heating time by temperature. Here, two factors must be considered: the heat-penetration in the canned salmon and the environmental temperature (in retort).

In the inspection of canned salmon by organoleptic examination the hardness of the backbone which is considered to be satisfactory for eating, is called "optimum hardness of bone". That is 6 kg/cm^2 from the analysis of the experimental results which were obtained by Matsuike *et al*[18]. Time required to soften the backbone of kinds of salmon under the processing of various values of temperature-time is shown in Table 17.

Table 17. Time required to soften the backbone of kinds of salmon under the processing of various values of temperature-time

Heating at \ Fishes	Pink salmon	Chum salmon
5 *lbs* press. (227.2°F)	90 min.	40～60 min.
10 *lbs* press. (239.4°F)	40	25
15 *lbs* press. (249.7°F)	20	10

The curve showing the relation between the time required to soften the backbone and the processing strength (temperature-time) is called "thermal softening time curve". The reciprocal of value of time required to reach optimum hardness of bone is called "the softening rate value".

Here, the softening rate values of canned chum salmon (*Oncorhynchus keta*) under various processing temperature-times are shown in Table 18.

Table 18. Relation between "the softening rate value" of backbone and the processing temperature in the canned salmon

Heating time (min.)	8 *lbs* pressure	10 *lbs* pressure	12 *lbs* pressure	14 *lbs* pressure	16 *lbs* pressure
10	0.000	0.000	0.000	0.000	0.060
20	0.000	0.000	0.020	0.075	0.332
30	0.095	0.160	0.245	0.311	0.604
40	0.255	0.350	0.345	0.621	1.094
50	0.435	0.570	0.601	0.946	1.602
60	0.616	0.790	0.877	1.322	2.122
70	0.816	1.026	1.171	1.608	2.542
80	1.020	1.266	1.471	1.900	3.062
90	1.222	1.506	1.771	2.192	3.582

6. Relation between "the softening rate value" of backbone and the processing temperature with consideration of heat-penetration in the canned salmon

As the backbone is surrounded by a thick layer of meat in the canned salmon, it requires a long time to bring the temperature of the center of the bone to that of the retort. Here, the temperature of the center of the canned salmon is assumed to be that of the center of the backbone.

If the relation between the heat-penetration and "the softening rate value" is known, the time required to reach "the optimum hardness of bone" can be calculated in the processing of canned salmon.

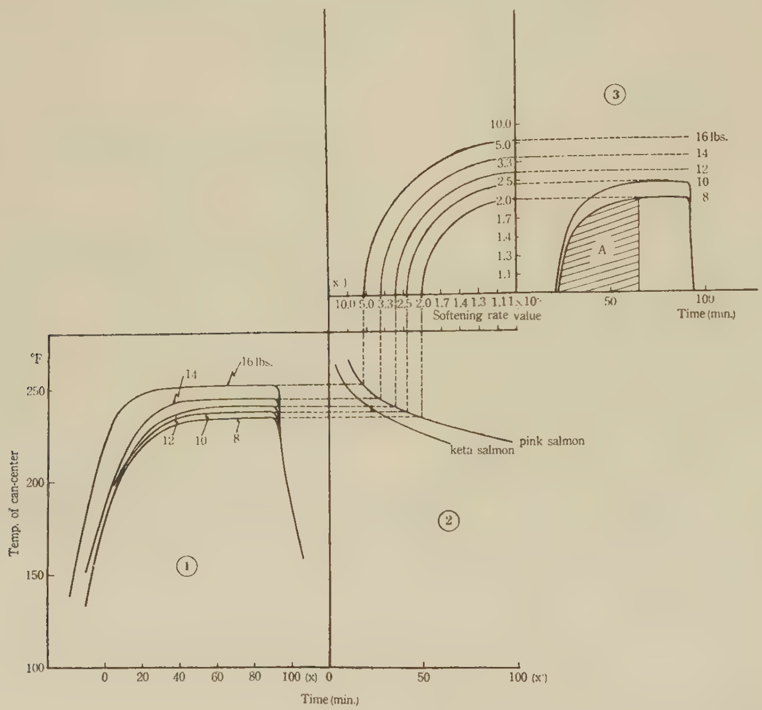


Fig. 14. A diagram showing the relation between "the softening rate value" of backbone and the processing temperature with consideration of heat-penetration in the canned salmon

Fig. 14 (1) shows the heat-penetrations curves of the canned salmon processed at 112.7°C (234.8° F, 8 *lbs* press.), 115.2°C (239.4°F, 10 *lbs* press.), 117.6°C (243.7°F, 12 *lbs* press.), 119.9°C (247.8°F, 14 *lbs* press.) and 122°C (251.6°F, 16 *lbs* press.). In Fig. 14 (2), which is placed side by side with Fig. 14 (1), the processing temperature is plotted on ordinate with the same scale as above, against the time required to attain to "the optimum hardness of the bone" on abscissa (x'). Then the reciprocal of the time requried to reach "the optimum hardness of the bone" is plotted on the upper abscissa (x''). This shows "the softening rate value of the bone" in Fig. 14 (3).

In Fig. 14 (3), "the softening rate value of the bone" is plotted on ordinate against the processing time on abscissa. This forms the curve showing the relation between heating-time and "the softening rate value" (the softening rate value curve). If the area under the softening rate value curve is 1, the hardness of the backbone in the

canned salmon is adequate. Then, the area is known, whether the processing time at the given temperature is sufficient or not to soften the backbone can be determined. From Table 18 also, one can know the ratio of the hardness of backbone, which was processed in the canned salmon (chum salmon) at various processing temperature-times, to "the optimum hardness of bone." The data given in Table 18 are plotted as "the softening rate value" against the processing time, as shown in Fig. 15.

In Fig. 15, when from 1.0 of the point of "the softening rate value," a parallel line to the abscissa is drawn, the upper parts of the curves above the parallel line show above 1.0, and then the backbone becomes softened. For example, the softening rate value is above 1.0 at the heating of 16 *lbs* press. for 43 minutes, at 14 *lbs* press. for 51 minutes, at 12 *lbs* press. for 60 minutes, at 10 *lbs* press. for 68 minutes, and at 8 *lbs* press. for 82 minutes.

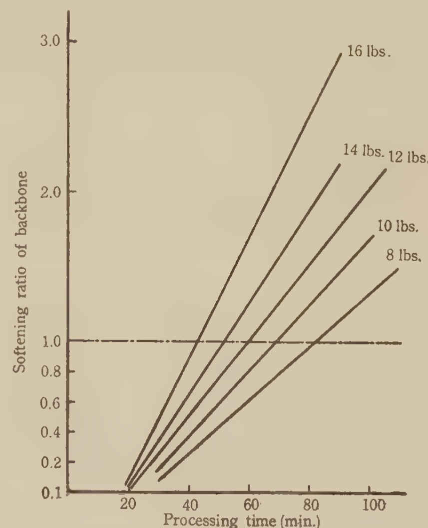


Fig. 15. The softening rate values of canned salmon under various processing temperature-times.

7. Relation among the processing time, thermal death time of bacteria and the number of bacteria attached to the raw material

Bigelow[12], Ball[13] and others have offered calculations of processing time required to obtain sterility in the canned foods. Bigelow's method is called the "general method", and Ball's method is called the "formula method". Their methods of calculation have contributed to the commercial processing of the canned foods in the U.S.A. Thereafter, Stumbo [14] has thought that the number of bacteria attached to the raw material and survival ratio are factors in the calculation of the processing time, because the thermal destruction curve of bacteria is logarithmic. He has offered the following equation showing the time "U" required to reduce the number of bacteria attached to the content of the canned foods to a definite aimed number of surviving bacteria.

$$U = Z\,(\log a - \log b) \quad \cdots\cdots\cdots\cdots \quad (7)$$

$$\text{or} \quad U = Z\,(\log a + P) \quad \cdots\cdots\cdots\cdots \quad (8)$$

Here, Z is the inclination of the thermal death curve at a definite processing temperature, "a" is initial number of bacteria per unit of the raw material of canned foods, "b" is the number of bacteria in the canned food after the processing. "P" is

logarithm of reciprocal of the number of the bacteria after "*U*" minutes. (Here, it is assumed $Z=1.225$ in Stumbo's calculation). Then, the processing time was calculated at various processing temperatures in the difference of the freshness of raw salmon meat. Here, as an object of the kind of the bacteria in the canned salmon, use was made of *Bac. megatherium*, which is a spore-forming bacterium and has been frequently isolated from the swelled canned salmon. The heat-resistance of the spores of *Bac. megatherium* is shown in Table 5 (p. 74). The relation between the decomposing velocity and the increase of the number of bacteria with the falling of the freshness of raw salmon meat should be discussed (Fig. 12).

According to the results previously obtained, the number of bacteria was 10^3 for fresh raw salmon meat (of which the amount of V.B.-N was below 10 *mg*%), 10^4 for rather fresh meat which is within the limit of freshness for raw material for the canned salmon (the amount of V.B.-N was 10~15 *mg*%), 10^5 for pretty unfresh meat (of which the amount of V.B.-N was 15~25 *mg*%), and 10^6 for unfresh meat in the stage of incipient putrefaction (the amount of V.B. -N was 25~39 *mg*%).

Here, the kind of bacteria attached to the raw salmon meat was assumed *Bac. megatherium* only, and the processing time required to reach 0.01[19] of survival number of bacteria in the canned salmon, taking the number of bacteria attached to the raw salmon meat into consideration, was calculated from Stumbo's equation. The processing temperature was 8, 10 and 12 *lbs* pressure between the highest and the lowest limits.

The results obtained are shown in Table 19.

In Table 19, the third column shows the calculated processing time assuming the bacteria attached to the raw meat to be *Bac. megatherium*. The fourth column shows

Table 19. The processing time at various temperatures in the difference of the freshness of raw salmon meat

Heating at	Number of bacteria attached	Calculated processing time (min.)		Processing time to which was added 20% of safety factor		Softening rate value of backbone at the safety processing time	
		Bac. megatherium	*Cl. botulinum*	*Bac. megatherinm*	*Cl. botulinum*	*Bac. megatherium*	*Cl. botulinum*
8 *lbs* (234.8 °F, 112.7 °C)	10^3	64.2	(78.2)	77.0	(94.2)	0.92	(1.23)
	10^4	65.7	(79.7)	78.8	(95.6)	0.95	(1.25)
	10^5	74.5	(88.2)	89.4	(105.8)	1.14	(1.41)
	10^6	80.8	(95.6)	97.0	(114.8)	1.28	(1.58)
10 *lbs* (239.4 °F, 115.2 °C)	10^3	60.5	(71.5)	72.6	(85.8)	1.07	(1.26)
	10^4	61.8	(72.5)	74.2	(87.0)	1.13	(1.40)
	10^5	65.7	(78.2)	78.8	(93.9)	1.22	(1.54)
	10^6	69.9	(81.0)	84.0	(97.2)	1.24	(1.64)
12 *lbs* (243.7 °F, 117.6 °C)	10^3	47.7	(68.2)	57.2	(81.8)	0.93	(1.53)
	10^4	48.8	(71.8)	58.7	(86.2)	0.97	(1.66)
	10^5	50.2	(72.5)	60.4	(87.0)	1.01	(1.69)
	10^6	52.7	(75.2)	63.2	(90.5)	1.03	(1.77)

the processing time assuming the bacteria to be *Cl. botulinum* which is more thermotolerant than *Bac. megatherium.*[14]

The fifth column shows the processing time to which was added 20% of safety factor[20], considering the rising velocity of temperature, or the kinds of bacteria attached to the raw material assuming the bacteria to be *Bac. megatherium.* The sixth column shows the processing time, assuming the bacteria to be *Cl. botulinum.*

The seventh and eighth columns show "the softening rate value of backbone" at each processing temperature-time assuming *Bac. megatherium* and *Cl. botulinum* respectively. When "the softening rate value" is above 1.0 the backbone becomes soft. Data in Table 19 are graphed as in Fig. 16.

From Table 19 and Fig. 16, the processing time at any definite processing temperature must be increased according to the freshness of the raw salmon meat (the number of bacteria attached). From Table 19 and Fig. 16, for example, if the bacteria are assumed to be *Bac. megatherium,* and if the processing temperature is 10 *lbs* pressure, the processing time is 73 minutes for the fresh meat. At this processing temperature and time, the backbone in the canned salmon becomes soft. Assuming the bacteria to be *Cl. botulinum,* the processing time is 86 minutes for fresh meat, 97 minutes for unfresh meat at 10 *lbs* pressure. At this processing temperature-time, the backbone becomes too soft.

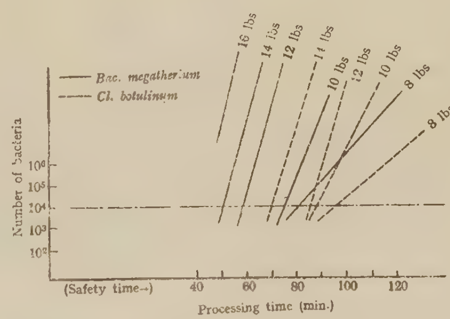


Fig. 16. Relations among the processing temperature-time, thermal death time of bacteria, the number of bacteria attached to the raw material and "the softening rate value"

8. Consolidated scale showing the relations among the leaving temperature-time of the raw salmon, falling of freshness and the processing temperature-time of canned salmon

Fig. 13 and Fig. 16 are put together in a consolidated scale as shown in Fig. 17.

In Fig. 17, if the temperature in the cannery is 25°C, the coefficient ("*p*") of the decomposing velocity in the initial stage is known to be 0.023. Then if the leaving time of the raw material is 20 hours after unloading into the cannery, the increase of V.B.-N is 2.0 and the number of bacteria is 10^4. If the number of bacteria is 10^4, the processing time is 73 minutes at 10 *lbs* pressure, and 59 minutes at 12 *lbs* pressure assuming *Bac. megatherium,* and 87 minutes at 10 *lbs* pressure, 86 minutes

at 12 *lbs* pressure assuming *Cl. botulinum.* In those processings, the backbone becomes soft. In this paper, a plan making consolidated scales for salmon canning by which the processing time is derived from the leaving temperature-time of raw salmon, was described. By use of such a plan for various kinds of fish, the same scale will be made. The scale may be convenient for the technologists of the cannery.

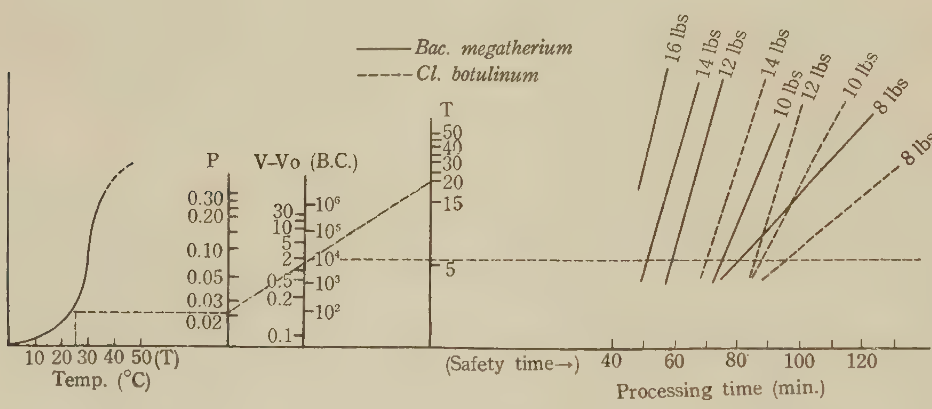


Fig. 17. A consolidated scale showing the relation among the leaving temperature-time of the raw salmon, falling of freshness and the processing temperature-time of canned salmon

VII. SMELL OF CANNED SALMON PREPARED FROM FROZEN MATERIAL

Salmon caught in Bering Sea is frozen and transported to the land canneries in Japan where it is prepared for the canned salmon. Those cans are said to have frequently some smell at the export inspection. The smell is called "freezing smell". The author has studied the cause of the formation of that smell.

1. Chemical components of the freezing smell in the canned salmon prepared from the frozen material

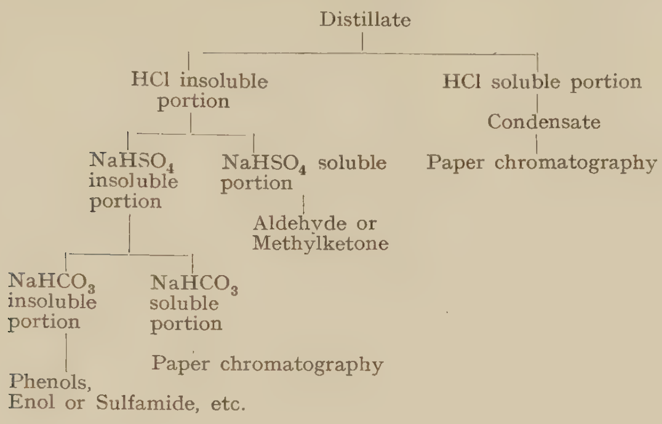
(1) *Experimental method*

After the opening of the canned product prepared from frozen salmon which was said to have the freezing smell, the content of the can was divided into the solid part and the liquid part. The solid part was distilled by steam for 40 minutes, and 220 *cc* of the distillate was obtained, of which the smell was the same as the freezing smell.

The distillate was fractionated as follows :

The detection of chemical components in each fraction in Scheme 1, was carried out by paper partition chromatography for bases and acids, and by reductive or iodo-

Scheme 1. Fractionation of the distillate obtained by steam distillation with canned salmon meat



form-reactions, diazo-reaction and color tests with fuchsin sulfite and dil. H_2SO_4 for aldehydes and methylketons.

For the detection of hydrogen sulfide which smelled strongly in the canned material the gas was absorbed by a detective tube in which silica gel was contained as an absorbent; then the absorbed hydrogen sulfide was proved by lead acetate.

(2) *Experimental results*

The results obtained are as shown in Table 20.

Table 20 shows also the results on commercial canned salmon prepared from fresh raw salmon. As seen in Table 20, from such canned salmon, hydrogen sulfide, cadaverine and formic acid were detected as odoriferous components; on the other hand, in addition to those three components, piperidine, acetic acid, formaldehyde and δ-aminovaleraldehyde were detected from the canned salmon which has the freezing smell. Those observations showed that the latter can had more kinds of components than the former can. That is to say, the causative odoriferous components were considered to be piperidine, acetic acid, formaldehyde and δ-aminovaleraldehyde etc.

Then, from where have those components come? Their formation is considered to be caused by the decomposition of amino acids from the fish meat protein with the falling of the freshness. In a later experiment, the author will prove this point.

2. Smells in the freezing storage chamber

The causes of the formation of odoriferous components are considered as follows: (1) the movement of the smell from the freezing storage chamber to the frozen salmon, and (2) the formation of the bad-smelling components by chemical change in salmon meat during the freezing storage.

Table 20. Components of the odor and chemical composition of canned salmon

Sample can	Volatile basic nitrogen (mg%)	Volatile acid (mg%)	Total nitrogen (%)	0.2% NaOH soluble nitrogen (%)	Ether extract (%)	Acid value	Saponification value	Iodine value	Peroxide-O_2 (%)	Components of the odor
Canned salmon, by fresh material	29.6	1.2	3.46	0.43	7.8	3.5	186.6	147.7	0.40	Hydrogen sulfide, Cadaverine, Formic acid
Canned salmon, by frozen fish (with a particular odor)	31.3	1.7	3.20	0.89	6.3	5.5	180.7	151.5	0.67	Hydrogen sulfide, Cadaverine, Piperidine, Formic acid, Acetic acid, Formaldehyde, δ-aminovaleraldehyde

In this experiment, in order to ascertain the cause, the detection of odoriferous components in the freezing storage chamber was carried out. There have been many studies of the smell concerning air conditioning of fruit storage chambers. But there have been few studies concerning fish storage. In studies on the chemical components of the smell of fruit storage chambers, an absorbent tube in which coconut palm shell charcoal was filled, has been employed[21].

(1) *Experimental method*

The present author has employed absorbent cotton, active alumina, Japanese acid clay, active charcoal as absorbents. The absorbent tubes were left in a freezing storage chamber in which many salmon were stored and in an empty storage chamber respectively for 3 months.

After 3 months' leaving of absorbent tubes, an absorbent tube of active charcoal was employed for the detection of the chemical components of the smell, because it absorbed smells most effectively among all absorbents used. The absorbents brought into the laboratory were treated as in Scheme 2.

Scheme 2. Treating procedure for an absorbent which absorbed the odor in refrigerating warehouse

Add petroleum ether to absorbent, and shaking

Repeat the treatment

Petroleum ether-soluble fraction

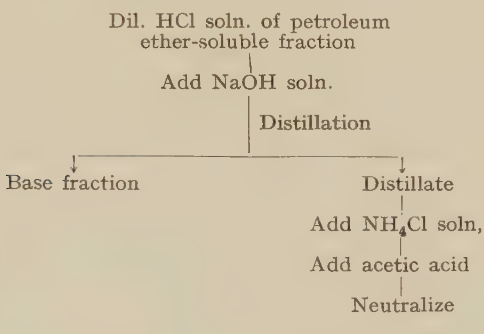
Petroleum ether-insoluble fraction

Wash absorbent two times with petroleum ether, then add water

In Scheme 2, a part of the fraction of petroleum ether-soluble substance was tested for the presence of nitrogen, with positive result. There-

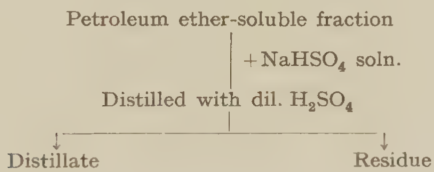
fore a small quantity of dil. HCl soln. was added to the fraction of petroleum ether-soluble, and shaken. This treatment was repeated several times. The whole solution was treated as in Scheme 3.

Scheme 3. Hydrochloric acid procedure for treating petroleum ether-soluble fraction



A part of the fraction of petroleum ether-soluble substance in Scheme 2 was taken and tested for reducing power. The test was positive. Therefore dil. sodium bisulfite solution was added to the rest of the fraction, and shaken, then treated as in Scheme 4.

Scheme 4. Sodium bisulfite solution procedure for treating petroleum ether-soluble fraction



Next, sodium bicarbonate solution wad added to petroleum ether-soluble substance, and shaken, and then dil. HCl solution was added. The solution was distilled. When dil. NaOH solution was added to petroleum ether-soluble substance and shaken, and dil. HCl solution added, no deposit was found, but the material smelled. In Scheme 4, petroleum ether-insoluble substance had no smell. This fraction was omitted from the further detections. The chemical components of substances of bases, aldehydes, acids or phenols obtained by those schemes were detected by paper partition chromatography. As the fraction of petroleum ether-soluble substance to which dil. NaOH solution was added and shaken, and then dil. HCl solution added, had no deposit, this fraction was not further detected. The bases obtained in Scheme

3 were changed to hydrochloride, and developed by one dimensional ascending chromatography. As developing solvent, *n*-butanol : acetic acid : water (3 : 1 : 2) was used, and as spraying reagent ninhydrin was used[22].

The chemical components of the smell in acidic substance were found to be lower molecular fatty acids. Therefore, hydroximate of volatile acids was synthesized and the hydroximate was developed with water-saturated *n*-butanol, and the spots developed were identified by saturated *n*-butanol with saturated ferric chloride solution[8].

In addition to volatile organic substance, it is considered that there are chemical components of so-called industrial gas in the smell of cold storage chamber. In order to identify the chemical components of the industrial gas, a detective tube (glass tube of dia. 4 *mm*, length 15 *cm*) was empolyed.

An analysis of industrial gas was made qualitatively.

When tests were made for phosphoretted hydrogen and hydrogen sulfide, as a detective tube containing copper sulfate and mercury chloride is changed to black color by hydrogen sulfide, two tubes were prepared. First one of the tubes was employed to absorb hydrogen sulfide, then the other to absorb phosphoretted hydrogen. The detective tubes were not affected by other gas components which were present[23] in mixed state.

As the carrier of the absorbents, silica gel granules were employed. For detection of sulfur dioxide, as absorbent, potassium bichromate was employed. For detection of ammonia, cobaltous chloride containing water; for detection of ethylene, palladium sulfate; for formaldehyde, a mixture of copper sulfate and mercury chloride were employed respectively.

(2) *Experimental results*

Basic substance obtained in Scheme 3 formed crystals of picrate, of which 3 kinds of chemical components were considered to be present. From the results obtained in paper chromatogram, there was revealed an area considered to be from the starting spot to the spot corresponding to cadaverine, but the separation of the three components was difficult. As the basic substance showed positive in the color reaction with paraquinone, chemical compound of piperidines were considered to be present in the basic substance. According to the shape of the crystals, the presence of piperidine, δ-aminovalerianic acid, reacted substance of the piperidine with acetaldehyde was supposed, but from the results in which those basic substances were dissolved by dil. HCl soln. and the substance which was dissolved by NaOH soln. was not detected, the presence of δ-aminovalerianic acid was uncertain. So cadaverine detected in paper chromatography was considered to be one of the components responsible for freezing smell.

In the empty storage chamber, as a control, no basic substance described above

was detected. Those basic substances were considered to be formed from the salmon stored in the freezing chamber. Obata[24] *et al.* have reported that they separated piperidines from the mucous substance of the surface of salmon, and this piperidine formed the fish smell.

The present author has detected piperidine-like substances in the smell components in the freezing storage chamber in which salmon was stored as above stated. If the precursor of piperidine is lysine, as Obata said, the presence of cadaverine as a decomposed intermediate substance can be considered to be reasonable.

Lysine ⟶ Cadaverine ⟶ Piperidine

In chromatography, the component in which Dragendorf's reaction was doubtful positive, was considered to be trimethylamine.

Chemical components obtained in treating of addition reaction between petroleum ether-soluble substance and sodium bisulfite as shown in Scheme 4, have reductive property, but negative was shown to the iodoform reaction. Therefore, the presence of aldehydes was confirmed, but methylketon was absent. When the distillate was taken on filter paper, and was subjected to ninhydrin reaction and diazo-reaction, those reactions were positive as indicated by red color. A part of the distillate was taken into a small test tube and the same amount of 50% NaOH solution and slight amount of resorcine were added. The test tubc was heated. As the solution changed slightly to yellowish red color, the reaction was doubtful positive.

The facts that the diazo-reaction was positive and the resorcine-reaction was doubtful positive, are considered to show the presence of formaldehyde and acetaldehyde. It is said that formaldehyde is formed, when trimethylamine changes to dimethylamine.[25] But in this experiment, it was uncertain.

Obata[24] has cited δ-aminovaleraldehyde and a substance formed from piperidine and acetaldehyde (1-1-bis-piperidine-ethane) as components of the fish smell. The fact as above stated that ninhydrine reaction was positive on filter paper, is considered to show the presence of δ-aminovaleraldehyde as a smell component. Acetaldehyde is also considered possibly to be formed in the reaction with piperidine. But formaldehyde and acetaldehyde except aldehydes which were positive in ninhydrin reaction were found in the empty freezing storage chamber, so the source of the formaldehyde and acetaldehyde is not considered to be only the chemical change of raw salmon meat.

Sodium bisulfite solution was added to petroleum ether-soluble substance and the mixture was shaken, dil. HCl solution was added and then preparate was distilled. The distillate was subjected to the detection of organic acids. Hillig and Clark[9] have found formic and acetic acids in the canned salmon meat. In the present author's experiment, amongst the chemical components of smell in the storage chamber in which salmon was stored, formic acid was detected, but acetic acid was not found.

On the other hand, in the empty chamber, the components of fatty acids were also not found. Therefore, acetic acid may be not formed, because the salmon was

frozen in the fresh condition. The chemical changes of fatty acids will be noted in a later experiment.

When the petroleum ether-soluble substance was shaken with dil. NaOH solution, to which dil. HCl solution was then added, slight bad smell was formed. As the components of the smell, a weak acidic substance should be separated. This substance may be methylmercaptan.

From the identification of the kinds of industrial gas by use of an absorbent tube ammonia, ethylene, hydrogen sulfide, phosphoretted hydrogen, formaldehyde and acetaldehyde were detected. It is uncertain whether formaldehyde is formed from salmon meat or from the atmosphere of empty freezing storage chamber. It is interesting that hydrogen sulfide and phosphoretted hydrogen were formed from the freezing storage chamber in which salmon was stored, but were not detected from the empty storage chamber. It has been already ascertained that hydrogen sulfide and phosphoretted hydrogen were formed in the raw salmon meat, so those components in the smell of freezing storage chamber may be formed from the frozen salmon material.

From the results above stated, as the chemical components of the smell in the freezing storage chamber, piperidines, trimethylamine-like substance, ammonia, ethylene, hydrogen sulfide, phosphoretted hydrogen, were proven. Those components were mixed and the smell of the freezing storage chamber may be formed by their interaction with each other.

As the chemical components of the smell in the empty storage chamber, industrial gases such as ammonia, ethylene, formaldehyde and acetaldehyde were detected.

3. Chemical changes of the fat and oil in salmon body which was frozen and stored

The author has observed that there is some smell in the freezing storage chamber in which raw salmon was stored, aside from the proper smell of the freezing chamber, and he considered that the smell may be formed from raw salmon meat. Here, as next described the author has studied the chemical changes of the fat and oil in salmon body during the storage and has tried to clear up whether a cause of the freezing smell may be a chemical component formed.

(1) *Experimental method*

The head was removed from salmon (of which the amount of V.B.-N was 7 *mg*%) caught near Hokkaido, and body was viscerated. Thus dressed salmon were frozen at –15°C and left in the cold storage chamber at the same temperature. Pretty unfresh salmon of which the amount of V.B.-N was 15 *mg*% was treated as the same way as fresh salmon.

In order to prevent the oxidation of fat and oil in salmon in the freezing storage, 0.008 *g* of "Sustane 1-F" (commercial name of Buthyrated hydroxyanisole was ap-

plied; this is a mixture of two isomers, 3-tert-butyl-4-hydroxyanisole and 2-tert-butyl-4-hydroxyanisole). The substanse was dissolved in 80 *cc* of ethanol and was made to 8000 *cc* by adding water. This makes 1/10,000 concentration of "Sustane 1-F". The fresh dressed salmon was soaked in 1/10,000 concentration of the solution for one hour. After the soaking, the salmon was taken up and drained. The material treated with "Sustane 1-F" was frozen at −15°C and stored.

At definite intervals of the leaving time, a part of each sample of salmon was cut, and crushed in a mortar. In order to extract the oil from the meat, according to Rachwood[26] *et al*, and Watts and Peng[27], to the crushed meat was added ether and Glauber's salt and extracted, then homogenized for 10 minutes in a blendor, of which the sides were cooled by ice.

The total amount of fat and oil in salmon body was estimated by extracting the oil from the crushed and dried salmon meat with ether in a Soxhlet's extractor.

Estimations of acid value and saponification value were carried out with the extracted oil as usual. Estimation of iodine value was made by Wijs' method. Estimation of the amount of peroxide oxygen was carried out as follows[28].

A certain weighed quantity of the extracted oil was dissolved by 50 *cc* of a mixture solvent made of mixed 6 volumes of glacial acetic acid and 4 volumes of carbon tetrachloride and then added 1 *cc* of saturated potassium iodide. And the material was left at cold dark place for 1 hour, and titrated with N/100 sodium thiosulfite solution. One *cc* of N/100 sodium thiosulfite solution corresponds to 0.00008 *g* of active oxygen.

(2) *Experimental results*

Results obtained are shown in Figs. 18∼22 .

Fig. 18 shows the variation of acid value of oil in salmon which was frozen and stored. As seen in Fig. 18, the acid value of oil in salmon frozen in very fresh condition increased gradually until 40 days of cold storage, but it kept constant value after 40 days. On the other hand, the acid value of oil in salmon frozen in unfresh condition (of which the amount of V.B.-N was about 15 *mg*%) increased gradually even after 100 days of cold storage. The acid value of oil in fresh salmon (of which the amount of V.B.-N was about 7 *mg*%) to which "Sustane" was added, and was frozen, increased gradually in the initial stage, but was not increased as a result of addition of "Sustane" even after 100 days' storage, showing below 2.08

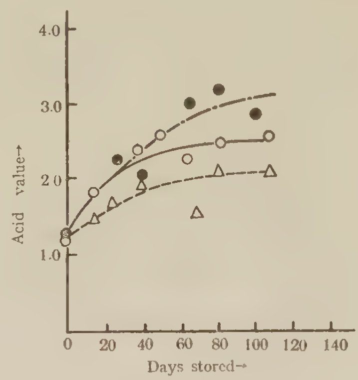


Fig. 18. Changes in the acid value of salmon oil during cold storage
——o—— Fresh salmon in initial quality
---•--- Unfresh salmon in initial quality
----Δ---- Frozen salmon treated with "Sustane 1-F"

value. From those results, the oxidation was observed to increase, in initial stage, in oil of salmon frozen even at fresh condition. On the other hand, the oxidation was observed to increase remarkably in oil of salmon frozen in unfresh condition. The increase of the acid value is an index of the increase of the amount of free fatty acids in oil, so it is possible that the acid value increases in the initial stage of the cold storage, but it does not increase in final stage, owing to the polymerization or combination with other chemical components except free fatty acids as Satodate[29] has stated.



Fig. 19. Changes in the saponification value of salmon oil during cold storage (See Fig. 18 as to the different marks).

Fig. 19 shows the variation of the saponification value of oil in salmon of which the freshness was changed, and in salmon to which "Sustane 1-F" was added. The tendency of the variation of saponification value showed almost the same as that of the acid value. The saponification value of oil in salmon which was frozen fresh or unfresh, or to which "Sustane 1-F" was added, decreased until 40 days' cold storage and onward in contrast with the acid value, increase in the middle stage, and decreased in final stage. These facts may be considered to be due to the reason that during the cold storage, the total amount of fatty acids decreases owing to the oxidative decomposition of fat and oil in salmon at initial stage, but the oxidative decomposition may be stopped with the elongation of the storage period; the total amount of fatty acids begins to increase, and with lengthening of time the accumulated amount of fatty acids decreases through the decomposing progress such as autoxidation.

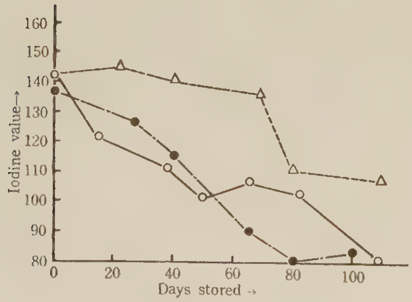


Fig. 20. Changes in the iodine value of salmon oil during cold storage (See Fig. 18 as to the different marks).

Fig. 20 shows the variation of the iodine value during the cold storage of frozen salmon. The value decreased gradually with the lapse of time. The iodine value of fat and oil in salmon frozen fresh or unfresh decreased with the same tendency, but that in salmon to which "Sustane 1-F" was added decreased comparatively slowly. The decrease of the iodine value during cold storage may be due to the increase of the absorption of oxygen in view of considering from the increase of the acid value.

According to Lovern[30], the kinds of fatty acids in salmon body oil include my-

ristic acid (C_{14}), palmitic acid (C_{16}), stearic acid (C_{18}) as saturated fatty acids and zoomaric acid (C_{16}), oleic acid (C_{18}), gadoleic acid (C_{20}), cetoleic acid (C_{22}) as unsaturated fatty acids. The larger amount of fatty acids is occupied by those, of which the degree of unsaturation is comparatively higher. Therefore, the fat and oil in salmon body is considered to oxidize and to form oxide and peroxide. In order to confirm the tendency, the variations of the amount of peroxide-oxygen formed and the amount of the ether-extracted matter during cold storage were observed. The results obtained are shown in Figs. 21 and 22 respectively.

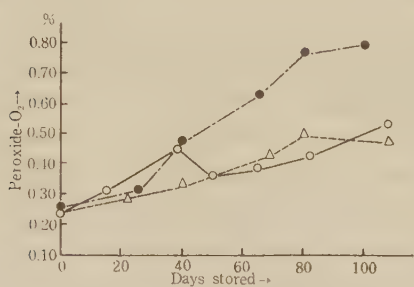


Fig. 21. Changes in the amount of peroxide-oxygen of salmon oil during cold storage (See Fig. 18 as to the different marks).

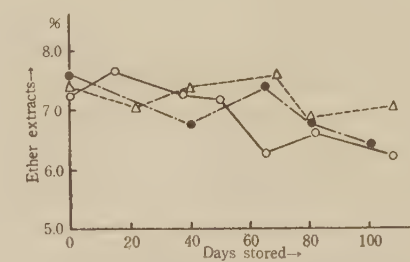


Fig 22. Changes in the amount of ether-extract from frozen salmon meat (See Fig. 18 as to the different marks).

As seen in Fig. 21, the amount of peroxide-oxygen increased with the passage of the storing time. The amount formed was the largest in salmon frozen in unfresh condition. The amounts formed were as great in salmon frozen in fresh condition and in salmon to which "Sustane 1-F" was added. But the amount in salmon to which "Sustane 1-F" was added, decreased in the final storage period. This fact may be due to the decomposition of the formed peroxide, as seen in the variation of the acid value.

As seen in Fig. 22, the amount of peroxide-oxygen kept constant after 50 days' storage of salmon freshly frozen, and decreased in the final stage. The amount in salmon, to which "Sustane 1-F" was added, kept constant after 70 days' storage, and decreased thereafter. This fact may be due to the absorption of oxygen in the air in the initial stage, and the decomposition of oxide or peroxide formed by the absorption in the final stage. For comparison of the acid value, saponification value, iodine value which were obtained by Toyama[31] in oil of chum salmon with that of the

Table 21. Properties of the salmon oils

Sample No.	Acid value	Saponification value	Iodine value	Researcher
1	2.21	187.9	131.5	Toyama
2	4.11	188.9	128.3	
3	2.69	191.4	144.1	
4	1.23	181.2	142.2	Authors

present author, the data are shown in Table 21.

As seen in Table 21, the results obtained by the present author agreed with Toyama. According to Hirose[32], the iodine value is 140～160 and the saponification value is 180～190 in commercial chum salmon oil. The fact that the acid value obtained by the present author was smaller than Toyama's, may be due to the non-performance of hot extraction in the oil extraction from salmon body.

It has been said that the antioxidant of "Sustane 1-F" is effective upon unsaturated fatty acids and their glycerides. Therefore, it was considered to be effective for salmon oil which has comparative larger amounts of unsaturated fatty acids. In fact, in this experiment the oxidation of oil of salmon, to which "Sustane 1-F" was added, was observed to be prevented more effectively than that in salmon to which no "Sustane 1-F" was added. This effect was not sufficiently observed in the initial stage, but was clearly observed with the increase of the storing period. This may be due to the reason that "Sustane 1-F" will absorb activated energy of peroxide formed in oil or will break down the chain reaction of molecules of unsaturated fatty acids in oil, as Filer *et al*[33], Lundberg *et al*[34], and Mahon and Chapman [35] have said.

From the results obtained, even if salmon was frozen and stored at –15°C, the fat will change chemically, though the change may be slow.

The fat and oil of salmon is hydrolysed to fatty acids and glycerine under the presence of water moisture and oxygen in the cold storage chamber; among fatty acids, higher molecular fatty acids decompose to lower molecular fatty acids and aldehydes, which perhaps become components of "the smell of the freezing chamber".

4. Variation of the amount of various kinds of nitrogen of salmon which was frozen and cold stored

In this experiment, in order to learn the chemical chahges of meat protein of salmon, from which the chemical components of "the smell of the freezing chamber" will be formed, the author has clarified the phenomenon of "meat burn", a kind of chemical change of stored fish meat.

The denaturation of the meat protein of salmon which was frozen and cold stored was studied by Tadokoro and Watanabe[36]. According to their results, the amounts of total nitrogen and of NaCl solution-soluble nitrogen decreased, and the amounts of free amino acid nitrogen increased as a result of freeze-storing. Satodate[29] has studied the chemical change of meat protein of fish meal stored at room temperature under various conditions and observed that even in meat protein molecules, unsaturated radicals combine with oxygen and the oxidation proceeded; he has estimated the degree of the oxidation by the solubility by alkali solution.

(1) *Experimental method*

Salmon which was frozen and cold stored was employed as in the previous ex-

periment.

The amount of total nitrogen was estimated by the micro-Kjeldahl method. The amount of amino acid nitrogen was estimated by Pope-Stevens' method. The amount of volatile basic nitrogen was estimated by Weber and Wilson's method. The amount of cold water-soluble nitrogen was estimated by using 10 *cc* of the extract obtained by extracting the sample of salmon meat with 10-fold volume of water and stirring for 40 minutes. The amount of alkali solution-soluble nitrogen was estimated by the same method, by extracting with 0.2% NaOH solution.

(2) *Experimental results*

Results obtained are shown in Table 22 and Figs. 23~27. Table 22 shows the variation of the amounts of total nitrogen and 0.2% NaOH solution-soluble nitrogen in

Table 22. Changes in the solubility of the salmon meat caused by the alkali solution

Samples	Nitrogen dissolved	Days stored						
Fresh salmon in initial quaiity		0	15	38	50	65	82	108
	Total-N	2.98	3.12	3.19	3.16	3.03	2.81	2.78
	Alkali soluble-N	0.47	0.42	1.15	1.84	1.84	1.69	1.67
	Solubility*	15.77	13.46	36.05	58.23	61.39	60.14	60.07
Unfresh salmon in initial quality		0	27	40	65	80	100	
	Total-N	3.17	3.24	2.95	3.09	3.04	2.78	
	Alkali soluble-N	0.56	0.55	1.31	1.24	1.95	1.83	
	Solubility*	17.67	16.98	44.41	40.13	64.14	65.82	
Sustane 1-F added salmon		0	22	40	69	80	108	
	Total-N	2.98	3.06	2.90	2.92	2.88	2.93	
	Alkali soluble-N	0.47	0.57	0.80	1.07	1.69	1.72	
	Solubility*	15.77	18.63	28.97	36.64	58.67	58.70	

* Ratio of 0.2% NaOH solution-soluble nitrogen for total nitrogen.

salmon of which freshness is different and to which "Sustane 1-F" was added, and the variation of the solubility which is indicated by the ratio of 0.2% NaOH solution-soluble nitrogen to total nitrogen.

Fig. 23 shows the variation of the solubility of salmon meat for 0.2% NaOH solution during the freezing-storage. As seen in Table 22, the amount of total nitrogen decreased with the continuation lapse of the storing; on the contrary the amount of 0.2% NaOH solution-soluble nitrogen increased. Therefore, as seen in Fig. 23, the solubility of 0.2% NaOH solution-soluble nitrogen increased gradually. In each sample, the variations were not remarkable until 20~30 days of freezing-storage;

thereafter the solubility in each sample increased until 50~80 days, and the variation kept constant after 80 days of storing. According to the variation of the solubility, the meat protein was oxidized and was considered to have been converted to oxyprotein. But the degree of oxidation was not necessarily the same in each sample, and oxidation did not occur in the same proportion throughout the storing period. The variations of the solubility in salmon which were frozen in fresh condition and in unfresh condition were almost the same, so the degree of the oxidation of the meat protein may be said not to be remarkably influenced by the freshness. In salmon to which "Sustane 1-F" was added, the oxidation of the meat protein was considered to be prevented to some degree in comparison with salmon to which no "Sustane 1-F" was added; further, the solubility was small throughout the storing period. The observation of a small decrease in the amount of total nitrogen in each sample with the lapse of the storing time, may be interpreted by the loss of the amount of nitrogen in volatile matters. This agrees with the finding of Tadokoro and Watanabe[36].

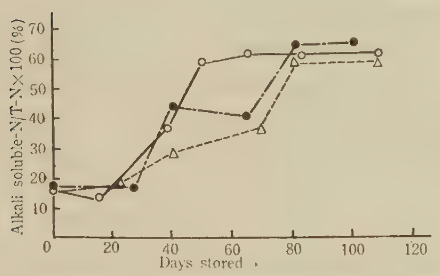


Fig 23. Changes in the solubility of the salmon meat caused by the alkali solution
—o— Fresh salmon in initial quality
-—o—- Unfresh salmon in initial quality
----Δ---- Frozen salmon treated with "Sustane 1-F"

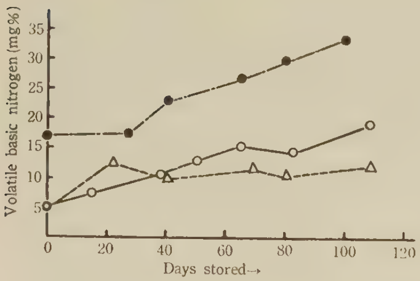


Fig. 24. Changes in the amount of volatile basic nitrogen in salmon meat during cold storage (See Fig. 23 as to the different marks)

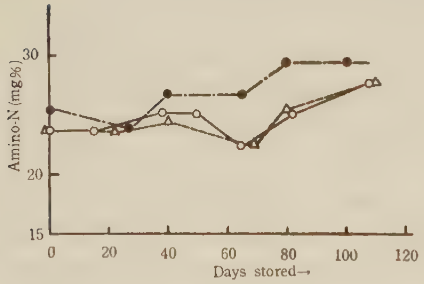


Fig 25. Changes in the amount of amino acid nitrogen in salmon meat during cold storage (See Fig. 23 as to the different marks)

Fig. 24 shows the variation of the amount of volatile basic nitrogen during the freezing storage. As seen in Fig. 24, the amount of volatile basic nitrogen in each sample increased remarkably. Salmon meat protein decomposes to lower molecular bases. Such bases as cadaverine and piperidine which were found in the smell of freezing chamber were considered to come from the decomposition of salmon meat. In salmon meat frozen unfresh, the amount of the volatile

basic nitrogen increased remarkably during freezing storage.

On the other hand, the amount increased less in salmon frozen fresh. The increase in salmon to which "Sustane 1-F" was added, was lower than that was not added. This may be due to the fact that the addition of "Sustane 1-F" prevents the oxidic decomposition of salmon meat protein.

Fig. 25 shows the variations of the amount of amino acid nitrogen during the freezing storage. As seen in Fig. 25, the amount of amino acid nitrogen increased gradually. This may be due to the slow decomposition of salmon meat protein by autolysis during the storage.

Fig. 26 shows the variation in the amount of water-soluble nitrogen of salmon meat. As seen in Fig. 26, the amount of water-soluble nitrogen increased until 50 days' storage in salmon meat which was frozen in fresh condition, until 65 days' or 70 days' storage in salmon meat frozen in unfresh condition or in salmon to which "Sustane 1-F" was added, respectively; and then the amount decreased in each sample.

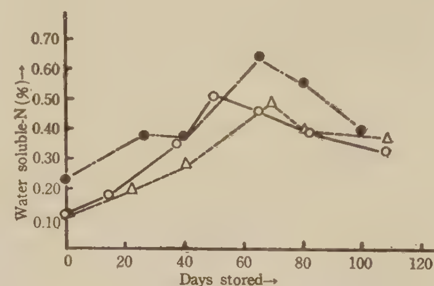


Fig. 26. Changes in the amount of water-soulble nitrogen in salmon meat during cold storage (See Fig. 23 as to the different marks)

Owing to the decomposition of meat protein, it seems to be right that the amount of water-soluble nitrogen increased in the initial stage. But the decrease in the final stage may be explained by the amino-carbonyl reaction (Maillard's reaction[37]). The browning of dried vegetables, dried egg, powdered milk and condensed milk is explained by this reaction. Further, Tarr[38] has clarified the browning of marine foods by this reaction. But this reaction can explain not only in the browning of foods, but also in the decrease of flavour, or the formation of unpleasant smell. This reaction accompanies the decrease of the solubility and pH value of the meat protein, and the formation of fluorescence by the radiation of ultraviolet ray.

The increase of pH value of salmon meat, as seen in Fig. 27, was observed in the initial stage, but in the final stage decrease was observed accompanying with the decrease of the amount of water-soluble nitrogen. When each sample of salmon was subjected to ultraviolet ray, no fluoresence was observed in each sample in the intial period of the storage, but after 70 days' storage it was observed near

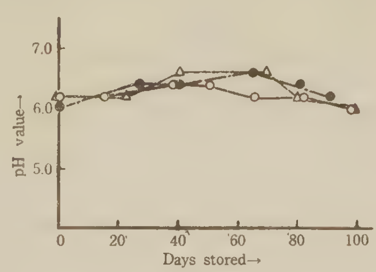


Fig. 27. Changes in the pH value in salmon meat during cold storage (See Fig. 23 as to the different marks)

belly part and near the part of reddish meat ("chiai-meat"). This fluorescence became remarkable with the lapse of the storing time.

According to the above observations, the amounts of various nitrogenous substances varied, that is to say the formation of oxyprotein, and the increase of volatile basic nitrogen and amino acid nitrogen owing to autolysis or oxidic decomposition were observed to occur. But those variations were slight. Therefore, those changes of chemical components were considered to affect more slightly to "the smell of freezing chamber" of salmon than changes in chemical components of the fat and oil decomposed by oxidation or hydrolysis. If "the smell of freezing chamber" is owing to the decomposition of salmon meat, the fatty substance may take a more important role than the decomposing substances of fish meat protein.

5. Volatile substances formed in salmon meat during the freezing storage

The author has detected the chemical components of "the smell of freezing chamber" in which salmon was stored, and observed the presence of piperidine, cadaverine, trimethylamine, formic acid, δ-aminovaleraldehyde, mercaptane-like substance, ammonia, ethylene, hydrogen sulfide, phosphoretted hydrogen; further, bases, acids and aldehydes among those components were considered to be formed from fat and oil or protein by the autolysis or decompoistion which took place during the freezing-storage. In this experiment, the formation of volatile bases and acids was observed.

(1) *Experimental method*

As samples, salmon frozen fresh or unfresh, and to which "Sustane 1-F" was added, was employed. For the detection of volatile bases, 50 *g* of each sample of salmon meat was taken into flask, added 10% NaOH solution and steam distilled. The distillate was received into a flask in which 2 *cc* of 1N HCl solution was added. After 40 minutes' distillation, the distillate was almost dried on water-bath. To the dried substance water was added to make 1 *cc*. Then the solution was employed for paper chromatography. The spraying reagent was ninhydrin. For the detection of volatile acids, they were esterificated by Fink and Fink's method[8]. Potassium hydroxamate thus obtained was subjected to the paper chromatography as described in the previous experiment.

(2) *Experimental results*

Results obtained are shown in Table 23. The variation of the amount of volatile acids is shown in Fig. 28. As seen in Table 23 and Fig. 28, the amount of volatile acid increased with the lapse of the storing time. This fact has been reported by many investigators. It may be due to the decomposition of higher molecular fatty acids or reductive decompsotion of amino acids in the meat. The increase of the amount

Table 23. Changes in the amounts of volatile basic nitrogen and volatile acid in salmon meat during cold storage

Samples	Volatile matters	Days stored						
		0	15	38	50	65	82	108
Fresh salmon in initial quality	V.B.-N (*mg%*)	5.0	5.5	10.1	13.8	15.3	14.4	19.2
	Volatile acid (*mg%*)	0.3	0.4	0.6	0.7	1.7	1.7	2.8
		0	27	40	65	80	100	
Unfresh salmon in initial quality	V.B.-N (*mg%*)	17.0	17.8	23 0	26.8	30.0	33.4	
	Volatile acid (*mg%*)	0.1	0.8	1.4	1.7	2.5	3.1	
		0	26	40	69	80	108	
Sustane 1-F added salmon	V.B.-N (*mg%*)	5.0	12.3	10.0	11.7	10.8	12.5	
	Volatile acid (*mg%*)	0.3	0.8	0.8	1.3	1.5	2.6	

of volatile acids in salmon frozen in unfresh condition was larger than that in salmon frozen fresh. The increase in salmon to which "Sustane 1-F" wad added, was the same as in freshly frozen salmon. The decomposition of the chemical components of the salmon was prevented, as Mahon and Chapman[35] said, so the increase was small. Figs. 29 and 30 show the chemical components of volatile bases and acids respectively which were identified by paper chromatography. The number of chem-i cal components increased with the falling of the freshness, and higher molecular substances appeared; those observations agrees with that of Hillig and Clark[9]. The period of appearance of chemical components of volatile bases or acids in salmon, to which "Sustane 1-F" was added, was later in salmon frozen when fresh.

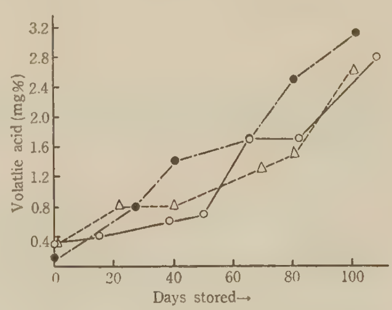


Fig. 28. Changes in the amount of volatile acid in salmon meat during cold storage (See Fig. 23 as to the different marks).

The author has already detected cadaverine, piperidine, trimethylamine as volatile bases in "the smell of freezing chamber" as shown in the previous experiment. In this experiment, agmatine and amylamine were detected from the salmon which was frozen unfresh, besides the three above noted bases.

From salmon frozen in fersh condition, or to which "Sustane 1-F" wad added, cadaverine was observed, but piperidine, agmatine and amylamine were not found.

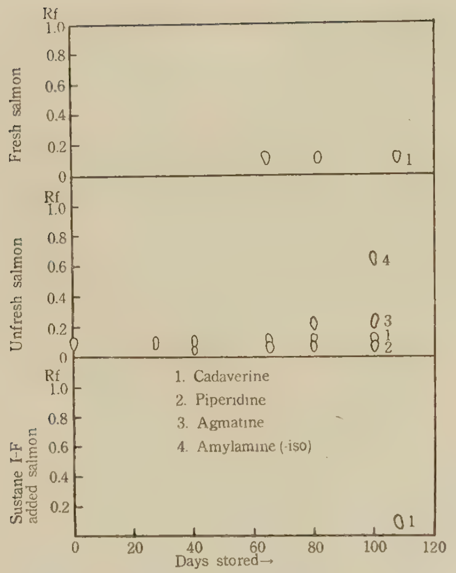


Fig. 29. Variations of the component of volatile bases in salmon meat during cold storage

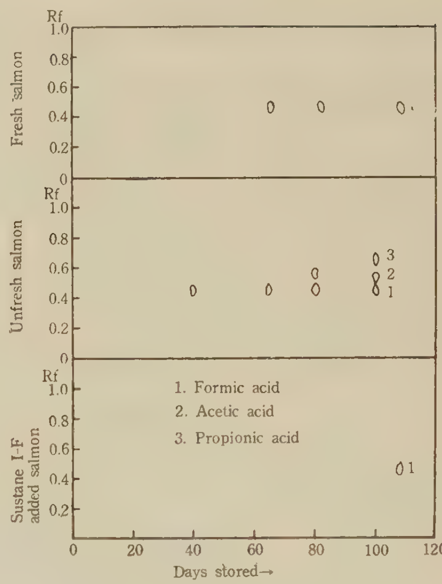


Fig. 30. Variations of the component of volatile acids in salmon meat during cold storage

Formic acid as a volatile acid was detected in "the smell of freezing chamber" in which salmon was stored. In this experiment, this component was detected in the final stage. This may be formed after the decomposition of the meat and it may have made "the smell".

It is not yet clarified whether the volatile bases and acids which were detected in raw salmon are introduced into canned salmon, or not. But during the processing of the canned foods, the amounts of volatile bases or acids do increase. Further, with the lapse of the storing time of frozen salmon, the amount and kind of the volatile bases and acids increase, especially in salmon frozen unfresh. Therefore, the storing time of frozen salmon should be less than 50 days judging from the amount and kind of volatile bases and acids which are formed. And unfresh material of raw salmon should not used for the canned salmon.

6. Quality of the canned product prepared from raw salmon, to which "Sustane 1-F" was added

The author has made it clear that the smelling of canned salmon prepared from frozen salmon was mainly due to the oxidation of the fat and oil in the material and that the addition of "Sustane 1-F" prevented the oxidation. In this experiment, the influences of the addition of "Sustane 1-F" upon the quality of the canned salmon were examined.

(1) *Experimental method*

Fresh salmon soaked in "Sustane 1-F" solution of 1/10,000 concentration was frozen and stored. After 50 days or 100 days of the storage, the salmon was prepared for canning as usual. In this case, salmon which was not soaked was also prepared for canning for the sake of contrast. The processed cans were incubated at 37°C for 2 weeks.

After the opening of the cans, the content was divided into the liquid part and the solid part. The solid part was employed for the estimation. From that part, oil was extracted. The extracted oil was employed for the estimation of the acid value, iodine value, saponification value and peroxide-oxygen. A part of the solid meat was employed for the estimation of the amounts of volatlie basic nitrogen, total nitrogen, water-soluble nitrogen and 0.2% NaOH solution-soluble nitrogen. In order to detect the smell of the canned salmon, the solid meat was steam distilled for 40 minutes, and 200 *cc* of the distillate was treated as in Schemes 1～4 described above in Experiment **1, 2** in this Chapter. Then it was employed for paper chromatography.

(2) *Experimental results*

Chemical components of the raw salmon and canned salmon were compared as shown in Table 24.

As seen in Table 24, the amounts of chemical component of canned salmon which were prepared from 100 days' storage were larger than those from 50 days' storage. This may be due to the decomposition of salmon meat by longer storage. The properties of salmon oil differed in cans which were prepared from raw salmon stored for varying periods. The acid value and the amount of peroxide-oxygen showed larger in canned salmon which was prepared from raw salmon of longer storing than from that of shorter storing. This may be due to the oxidation of the oil during the storage period.

Those facts were clearly explained not only from the results obtained in respect to the variation of properties of oil or the amount of various nitrogenous compounds in raw salmon formed during freezing storage, but also from results obtained in the use of canned salmon.

That is to say, the longer the frozen raw salmon is stored, the more clear the difference is. The formation of aldehydes or volatile acids from the oxidation of salmon oil having large amount of unsaturated fatty acids can be prevented by the treatment with "Sustane 1-F".

The canned salmon prepared from raw frozen salmon, to which "Sustane 1-F" was added, and stored for 100 days showed better quality in smell, color of oil and in meat than the canned salmon not "Sustane" treated.

The smell of canned salmon prepared from the frozen salmon, to which

Table 24. Qualities of canned salmon prepared from the frozen

Items / Samples	V.B.-N (*mg*%)	Volatile acid (*mg*%)	Total nitrogen (%)	0.2% NaOH soluble-N (%)	Ether extract (%)
(1) Frozen material after 50 days of freezing storage (No sustane was added)	13.8	0.7	3.16	1.84	7.2
(2) Ditto (Sustane was added)	10.2	0.9	2.92	0.91	7.4
(3) Canned salmon prepared from frozen material of above noted (1)	28.5	1.8	3.26	0.79	6.8
(4) Canned salmon prepared from frozen material of above noted (2)	21.3	1.0	3.14	0.99	7.0
(5) Frozen material after 100 days of freezing storage (No sustane was added)	19.2	2.8	2.78	1.67	6.2
(6) Ditto (Sustane was added)	12.5	1.0	2.93	1.72	7.0
(7) Canned salmon prepared from frozen material of above noted (5)	38.6	2.8	3.1	0.62	8.1
(8) Canned salmon prepared from frozen material of above noted (6)	28.6	1.2	3.76	1.64	

"Sustane 1-F" was added and stored within 100 days was the same as that prepared by fresh raw salmon.

In the canned salmon prepared from frozen salmon, hydrogen sulfide, formic acid, cadaverine were formed, but in canned salmon prepared from the same material stored for 100 days, acetic acid was found besides the three components above mentioned, but no freezing smell was observed. Therefore, the addition of "Sustane 1-F" is considered to prevent indirectly the formation of the smell by antioxidation of oil. But if the raw frozen salmon, to which "Sustane 1-F" was added and stored for a longer period (above 100 days), was employed for canning, the quality of the canned salmon was considered to become worse.

From those results, the fact that the formation of "the freezing smell" in the canned salmon is prevented by the antioxidation of the oil, shows that the formation of the smell is mostly affected by the decomposition of oil, rather than of meat protein. Therefore, in order to prepare the good quality products of canned salmon, the frozen fresh salmon, to which "Sustane 1-F" was added, must be used as raw material.

materials, to which "Sustane 1-F" was added or not

Extracted oil				
Acid value	Saponification value	Iodine value	Peroxide oxygen (%)	Smell components
2.6	179.2	101.8	0.36	Hydrogen sulfide, Formic acid, Cadaverine, Piperidine, Acetic acid, Formaldehyde
3.2	180.5	140.8	0.37	Hydrogen sulfide, Cadaverine, Formic acid, Acetic acid
4.5	186.2	144.0	0.63	Hydrogen sulfide, Formic acid, Cadaverine, Piperidine, Acetic acid, Formaldehyde
3.9	181.3	141.8	0.51	Hydrogen sulfide, Formic acid, Cadaverine
2.6	169.3	81.9	0.54	Hydrogen sulfide, Cadaverine, Formic acid, Acetic acid, Piperidine Formaldehyde, Amylamine, δ-aminovaleraldehyde
2.1	168.1	107.9	0.48	Hydrogen sulfide, Cadaverine, Formic acid, Acetic acid
3.9	182.6	155.5	0.86	Hydrogen sulfide, Formic acid, Cadaverine, Acetic acid, Piperidine, Formaldehyde, Amylamine, δ-aminovaleraldehyde
2.34	169.6	140.6	0.50	Hydrogen sulfide, Formic acid, Acetic acid, Cadaverine

VIII. BLACKENING OF CANNED SALMON

When salmon is filled in white cans, the inner side of the can-body blackens. The blackening of canned salmon is different from that of canned crab or shell fish meat. In the canned crab or shell fish, the meat blackens with the development of the blackening of the inner side of the container. But in canned salmon, even if the inner side of the can body blackens, it is seldom that the meat becomes black. The degree of the blackening of the inner side of the can-body is classified into 4 : brown, brownish violet, bluish violet, bluish black (or violetish black), according to Kawaguchi and Kimoto[39]. Sato and Yoshihara[40] have observed that the blackening occurs after the processing, and increases during the storage in warehouses. They have made it clear that the black substance is tin sulfide. Kawaguchi and Kimoto[39] have said that hydrogen sulfide formed from salmon meat combined with tin of inner surface of can-body and yielded brown or brownish violet sulfide substances of the 1st or 2nd types as above stated. They have said further that the formed stannic sulfide among the sulfide substances is dissolved by ammonium sulfide formed in the salmon meat

during the processing and bluish black sulfide of the 3rd type may result.

The present author[41] has studied how the degree of the blackening of the inner side of can-body is affected by the amount of hydrogen sulfide. According to the results obtained, if a sample having 1.61 *mg* (per can) of hydrogen sulfide was heated at 115°C for 85 minutes in a white can, 1/2–pound flat, the color of the can became brown, if the amount was 3.44∼17.2 *mg*, the color was brownish violet; if the amount was 22.9∼34.4 *mg*, bluish violet, and above 43.5 *mg* ,blackish violet. When the solution including the amount of 22.9 *mg* of hydrogen sulfide was heated in a white can, the inner side of the container blackened. The blackening increased when the can was stored at 50°C.

The present author[41] has also studied the relation between the processing temperature or the pH value of the meat and the amount of hydrogen sulfide formed.

According to the results, when canned salmon was processed at 113.9°∼122°C (9 *lbs*∼16 *lbs* pressure), the amount of hydrogen sulfide formed increased remarkably at temperatures above 117.6°C (12 *lbs* pressure). In the relation between the pH value and the amount of hydrogen sulfide, the amount increased remarkably above pH 6.6. The author has stated that the upper limit of the processing temperature of canned salmon was about 117.6°C (12 *lbs* pressure). This statement is based on result of an earlier study. In this experiment, the author has tried to clarify the relation between the degree of the blackening of canned salmon and the freshness of the raw salmon used.

1. Difference in the amount of hydrogen sulfide between the blackened canned salmon and commercial canned salmon

At the export inspection, the remarkably blackened canned salmon is called the "blackened canned salmon". Here the comparison between the blackened and ordinary commercial canned salmon was made with the results as shown in Table 25.

As seen in Table 25, in the blackened canned salmon, the inner side of the can-body

Table 25. Comparison between the qualities of blackened and commercial canned salmon

Items \ Sample cans		Blackened canned salmon	Commercial canned salmon (control)
Vacuum (inch)		16.2	13.5
pH of meat		6.3	5.8
Water content of meat (%)		28.4	33.6
Color of meat		Yellowish brown	Normal
V.B.-N of meat (*mg*%)		38.4	27.0
Juice	Total amount (*cc*)	88.8	96.0
	Water content (*cc*)	81.6	67.0
	Oil (*cc*)	7.2	29.0
Color of liquid		Blackish brown	Reddish brown (Normal)
Smell		Smell of H_2S was remarkable	Fishy smell (Normal)
Discoloration of the inner side of can-body		Violetish black	Brownish violet

was violetish black, and the meat brown, the liquid blackish. On the contrary, in the commercial canned salmon the inner side of the can-body was brownish violet, and liquid was reddish brown.

(1) *Experimental method*

After the opening of both sorts of canned salmon, the amount of hydrogen sulfide of the content (in solid meat and liquid) was estimated by Almy's method[42]. After taking out the content, the tin plate of the empty can was cut; conc. HNO_3 (1 : 1) solution was put on it and the amount of the dissolved tin sulfide was estimated. Also the amounts of tin dissolved out into meat and liquid portions were estimated.

(2) *Experimental results*

The amounts of hydrogen sulfide in the content and in the blackened substance attached to the inner side of the can-body, are shown in Table 26.

Table 26. Total amounts of hydrogen sulfide in blackened and commerical canned salmon

Amount of H_2S / Sample cans	Total H_2S in solid meat and liquid (*mg*%)	Amount of H_2S reacted with tin in the inner side of can-body (*mg*)	Total amounts of H_2S in the sample can (*mg*)
Blackened canned salmon	13.56	6.73	20.29
Commercial canned salmon	5.56	5.9	11.46

As seen in Table 26, the amount of hydrogen sulfide was larger in the blackened can than in the commercial canned salmon. The greater part of hydrogen sulfide combined with tin of inner side of the can-body.

Table 27 shows the amount of tin dissolved out into meat and liquid in cans.

Table 27. Amount of tin dissolved out into meat and liquid portions in the cans

Sample cans / Parts	Blackened canned salmon	Commercial canned salmon
In meat	4.95 *mg*/100 *g*	4.66 *mg*/100 *g*
In liquid	8.16 *mg*/100 *g*	5.46 *mg*/100 *g*

As seen in Table 27, the amount of tin in the meat was almost equal in both blackened and commercial cans, but the amount was larger in the liquid of the former than in that of the latter can.

2. Relation between the degree of the blackening and the freshness of the raw salmon

The pH value of fish meat increases with the falling of the freshness. It was stated above that the yield amount of hydrogen sulfide increases with the increase of pH value.

(1) *Experimental method*

Fresh salmon caught near Hakodate was dressed and left at 25°C and the freshness was artificially varied. The degree of freshness of the samples is shown in Table 28.

Table 28. The degree of freshness of the sample meat of salmon

Freshness \ Sample No.	1	2	3	4	5	6	7
V.B.-N (*mg%*)	8.2	9.2	18.6	26.0	31.0	36.6	42.7
pH	7.0	7.3	7.3	7.4	7.5	7.6	7.8

Such salmon meat was prepared for canning as usual. At the opening of sample cans stored at room temperature in 50 days, the amount of hydrogen sulfide was estimated, and the degree of the blackening was investigated.

The total amount of hydrogen sulfide in the can was the sum of the amount of hydrogen sulfide in the meat and the amount absorbed by 2% lead acetate solution which was poured through a hole into the head space of the can.

(2) *Experimental result*

Results obtained are shown in Table 29 (p. 125).

As seen in Table 29, the amount of hydrogen sulfide was greater in the canned salmon which was prepared from the unfresh salmon. This is also stated by Almy[42]. When raw salmon, amount of V.B.-N 18.6 *mg*%, was processed for canning, the amount of hydrogen sulfide was 2.83 *mg* per can, and the inner side of the can-body became blackish violet. On the other hand, when raw salmon, amount of V.B.-N 26.0 *mg*%, was processed, the amount of hydrogen sulfide was 5.44 *mg* per can, and the blackening was remarkable. With the falling of the freshness, the blackening became more remarkable, and the meat became brown.

The present author has offered the opinion that the limit of the freshness of raw salmon for canning should be 20 *mg*% of V.B.-N. In this experiment, when raw salmon was used, of which the amount of V.B.-N was above 20 *mg*%, the blackening was remarkable. If the raw salmon in the stage of incipient putrefaction (amount of

Table 29. Relation between the amount of hydrogen sulfide produced and the blackening of canned salmon having various freshness in raw material

Sample No.	Freshness of raw material (V.B.-N) (*mg*%)	Condition after opening the cans: H_2S in contents (*mg*%)	Total H_2S in can container (*mg*/can)	Degree of blackening (inner side of tin-container): Can-body	Can-top	Can-bottom	Color of meat	Smell	pH	V.B.-N (*mg*%)	Fe (*mg*%)
1	8.2	1.36	2.52	Bluish violet	No blackening	Same as left	Good	Normal	6.8	36.9	—
2	9.2	1.36	2.52	Ditto	Ditto	Ditto	Ditto	Ditto	7.4	40.9	2.6
3	18.6	1.70	2.83	Blackish violet	Bluish violet, somewhat blackish violet	Same as left	Ditto	Ditto	7.8	44.8	3.0
4	26.0	1.43	5.44	Remarkable blackish violet	Blackish violet	Same as left	Browned	No good slightly	7.6	46.2	8.0
5	31.0	1.91	8.10	Ditto	Same as left	Same as left	Ditto	H_2S smell	7.7	47.0	8.1
6	36.6	2.62	11.7	Ditto	Ditto	Ditto	Ditto	Ditto	7.9	48.7	—
7	42.7	2.58	19.6	Ditto	Ditto	Ditto	Remarkable browned	NH_3 and H_2S smells	—	—	—

V.B.-N, 30 *mg*%) was prepared for canning, the blackening became more remarkable and the meat became brown. In that case the amount of hydrogen sulfide became greater in the can.

From those results, with the falling of the freshness of raw salmon, the blackening may be stated to become more remarkable.

3. Relation between the degree of the blackening and the storing temperature of canned salmon after the processing

It is considered that the storing temperature after the processing may affect the increase of the amount of hydrogen sulfide formed and the degree of the blackening.

(1) *Experimental method*

Fresh raw salmon was dressed and left at 25°C. Samples of varied freshness were taken. Fresh raw salmon, the amount of V.B.-N was 15.12 *mg*%, pH was 5.91 and pretty unfresh salmon, the amount of V.B.-N was 23.24 *mg*%, and pH 7.36 were processed for canning at 10 *lbs* pressure for 90 minutes and stored at 10°~15°C, 37°C and 50°C for 60 days respectively. At definite intervals of storing time, the total amount of hydrogen sulfide was estimated and the degree of blackening was observed.

Table 30. Relation between the degree of blackening and the storing temperature of canned slamon prepared from the fresh raw material

Days stored	Storing temp. (°C)	H_2S in meat (*mg*%)	Total H_2S in tin container (*mg*/can)	Degree of blackening: Can-body	Degree of blackening: Can-top	Degree of blackening: Can-bottom	Color of meat	Smell	pH	V.B.-N (*mg*%)
10	10～15	10.3	17.0	No blackening	Same as left	Same as left	Normal	Normal	5.96	39.6
	37	10.5	21.2	Violetish brown	Ditto	Ditto	Ditto	Ditto	6.10	40.6
	50	13.3	25.5	Bluish violet	Slightly bluish violet	Bluish violet	Slightly browned	Slightly H_2S smell	6.00	41.6
30	10～15	16.3	23.8	Violetish brown	No blackening	Same as left	Normal	Normal	6.90	40.9
	37	18.7	42.5	Bluish violet	Same as left	Same as left	Slightly browned	Ditto	6.80	44.2
	50	18.9	31.5	Remarkable bluish violet	Bluish violet	Blackish violet	Ditto	Slightly H_2S smell	6.95	42.0
60	10～15	21.0	43.0	Violetish brown	No blackening	Same as left	Normal	Normal	6.70	45.3
	37	22.0	46.5	Bluish violet	Violetish brown	Bluish violet	Slightly browned	Slightly H_2S smell	6.75	—
	50	21.6	46.1	Blackish violet	Same as left	Same as left	Browned	NH_3 and H_2S Smells	7.00	45.4

(2) *Experimental results*

Results obtained are shown in Tables 30 and 31.

As seen in Table 30 and Table 31, when the canned salmon prepared from the fresh or unfresh raw material was stored at comparatively higher temperature, the blackening was more remarkable than in that stored at lower temperatures. That is, a larger amount of hydrogen sulfide was formed at higher temperature storing than at lower temperature storing. The longer the storing time was, the more the amount of hydrogen sulfide formed. At the same storing temperature, the total amount of hydrogen sulfide and the degree of the blackening were larger in canned salmon prepared from unfresh salmon than in that prepared from fresh salmon.

When the degree of the blackening in the canned salmon according to the difference of the storing temperature and

Table 31. Relation between the degree of blackening and the storing temperature of canned salmon prepared from the unfresh raw material.

Days stored	Storing temp. (°C)	H_2S in meat (*mg*%)	Total H_2S in tin-container (*mg*/can)	Degree of blackening			Color of meat	Smell	pH	V.B.-N (*mg*%)
				Can-body	Can-top	Can-bottom				
10	10～15	13.9	21.6	Slightly violetish brown	No blackening	Same as left	Slightly browned	No good	6.30	—
	37	20.2	40.6	Remarkable bluish violet	Violetish brown	Remarkable bluish violet	Ditto	Ditto	6.00	35.3
	50	22.1	42.4	Remarkable blackish violet	Blackish violet	Remarkable blackish violet	Ditto	NH_3 and H_2S smells	6.20	45.4
30	10～15	18.3	37.0	Slightly violetish brown	No blackening	Same as left	Slightly browned	No good	6.75	39.2
	37	20.4	40.9	Remarkable bluish violet	Bluish violet	Remarkable bluish violet	Browned	Ditto	6.80	—
	50	23.8	44.5	Blackish violet	Same as left	Remarkable blackish violet	Ditto	NH_3 and H_2S smells	7.05	50.9
60	10～15	20.2	43.6	Slightly violetish brown	No blackening	Same as left	Slightly browned	No good	7.00	39.7
	37	20.4	47.9	Bluish violet	Slightly bluish violet	Bluish violet	Browned	Ditto	7.05	42.8
	50	21.0	48.0	Remarkable blackish violet	Bluish violet	Blackish violet	Ditto	NH_3 and H_2S smells	7.20	49.0

of freshness was compared, it was difficult to compare. But to state some conclusion, the factor of the freshness is considered to be more important than that of the storing temperature.

If the raw unfresh salmon was processed for canning and stored comparative higher temperature and for longer time, the degree of the blackening became more remarkable.

4. The blackening of canned salmon in enameled cans

When white cans are employed for canned salmon, the blackening occurred on the inner side of the container, and the meat became brown; if the blackening was very great, the meat became partly black.

The author has tried to study the relation between the degree of blackening and the using of enameled cans. Recently electric tin plate (E.T.) is employed for canning. As the tin layer of E.T. is thin, the E.T. is covered by C-enamel or resin-coatings etc.

There are two kinds of coated-cans, one is coated on the top and bottom, and another is coated on whole inner side.

(1) *Experimental method*

Fresh raw salmon meat, amount of V.B.-N 13.8 *mg*%, pretty fresh salmon meat, amount of V.B.-N 20.1 *mg*% and unfresh salmon meat, of which the amount of V.B.-N was 28.1 *mg*%, were prepared for canning. Those samples of salmon meat having various degrees of freshness were filled into white cans, coated-cans at top and bottom and wholly-coated cans respectively. After 2 months' storage of canned salmon prepared as above described at room temperature, the cans were opened and the degree of blackening was observed. The amounts of tin and iron in the content of the can were estimated. The amount of tin was estimated by iodometry after wet decomposition of the content with a mixed solution of perchloric acid and sulphuric acid. The amount of iron was estimated by Hollett's[43] and Tompsett's[44] methods.

(2) *Experimental results*

As seen in Table 32, the degree of the blackening differed according to the kinds of can-coating. In white can, the degree of the blackening became remarkable, brownish violet and bluish violet, with the falling of the freshness of the raw salmon sample. In cans coated at top and bottom, only the white tin plate of can-body blackened while the coated surface did not change. In wholly-coated can, no black part was observed, but greyish brown spots were seen.

The amounts of iron and tin in the content of canned salmon increased with the increase of the blackening owing to the falling of the freshness except in wholly-coated cans.

On the other hand, in wholly-coated cans the amounts of iron and tin in canned

Table 32. Blackening of canned salmon in several kinds of cans prepared from the raw materials having various degrees of freshness

Freshness of raw material (V.B.-N, *mg*%)	White can			Coated-can at top and bottom			Wholly-coated can		
	Degree of blackening	Fe (*mg*%)	Sn (*mg*%)	Degree of blackening	Fe (*mg*%)	Sn (*mg*%)	Degree of blackening	Fe (*mg*%)	Sn (*mg*%)
13.8	No blackening	2.6	—	No blackening	1.7	—	No blackening	1.3	—
20.1	Brownish violet	4.7	12.1	Brownish violet at only can-body	2.6	12.1	Greyish brown spots at only can-top	7.1	3.8
28.1	Bluish violet	8.0	48.0	Bluish violet at only can-body	6.2	25.6	No blackening	2.8	2.2

salmon having greyish brown spots on the surface of inner side, were larger than in samples showing no spot.

If there are pinholes or weak points on the inner side of the can (at which a thinner layer of coating appeared), the dissolved metals from the pinholes or weak points combines with hydrogen sulfide formed from the salmon meat and greyish brown spots are formed. So when there are no pinholes on the inner surface, no blackening is observed.

5. Chemical components of the blackened substance

There have been many studies concerning the blackened substance. If the brown and brownish black part on the inner side of the cans were observed under a microscope, the discolored part has tin surface which was not yet reacted, and it did not discolor homogeneously.

This shows the presence of crystals of tin which have not reacted with hydrogen sulfide on the tin plate.

If ammonia polysulfide was applied to the discolored part, the discolored part disappeared and bright tin surface appeared again. From those facts the brownish black substance was considered to be tin sulfide.

On the other hand, what substance is the blackened part, then ? If this blackened part was washed with water, the blackened part disappeared and the brown or brownish black part appeared. The black parts were distributed much on the inner sides of can-bottom and can-body, and less on the inner side of top. The black parts were much found also at the points to which salmon skin or meat had attached. According to the results obtained in the past, the brownish black part formed on the inner side surface, which was considered to be tin sulfide, was dissolved by ammonium sulfide which was formed from ammonia and hydrogen sulfide from the fish meat whereupon

iron surface appeared; then iron sulfide was considered to be formed. But sulfide is not dissolved by ammonium sulfide, but by ammonium polysulfide containing a large amount of sulfur. From salmon meat, hydrogen sulfide is not so much formed as to form ammonium polysulfide. After washing of the black sulfide substance, the discolored part which was considered to be tin sulfide appeared on the surface of tin plate, and this discolored part was not dissolved by dil. HCl solution (1 : 3). From those results, the black substance is not yet considered surely to be iron sulfide.

Here the author has observed whether the black sulfide substance is tin sulfide or iron sulfide by electron diffraction.

(1) *Experimental method*

The black, brownish black and violetish black parts of the inner side of the blackened canned salmon were estimated by electron diffraction.

(2) *Experimental results*

Electron diffraction patterns are shown in Figs. 31～33.

Fig. 31 shows the pattern of electron diffraction obtained from the standard gilded sheet. Fig. 32 shows the pattern obtained from the black part of inner side of can-

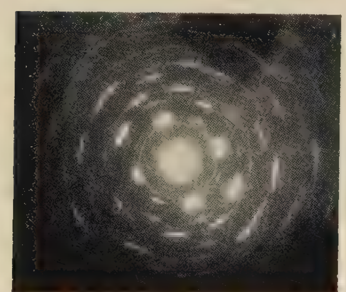


Fig. 31. A pattern of electron diffraction obtained from the standard gilded sheet

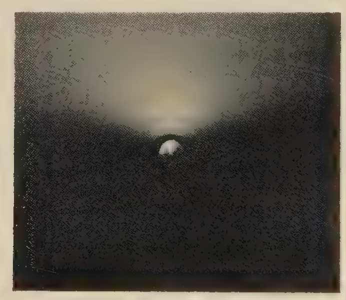


Fig. 32. A pattern obtained from the black part of inner side of can-body

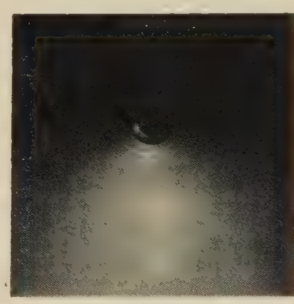


Fig. 33. A pattern obtained from the brownish black part of inner side of can-body

body, and Fig. 33 shows the pattern obtained from the brownish black part. The analyzed results of those patterns are shown in Table 33.

In Table 33, the results of SnS, FeS and FeS_2 tests are given. As seen in the table, the chemical component of the black part which was shown in Fig. 32 was considered to resemble SnS, and that of brownish black part which was shown in Fig. 33 was considered to resemble FeS_2.

As the crystals of the sample are very fine, and the breadth of the diffraction pattern was wide, the pattern was seen to be unique by naked eye, but it must be

Tabel 33. Analyzed results of the electron diffraction patterns

Black part		Brownish black part		FeS		FeS_2		SnS	
Lattice spacings d (Å)	Strength	Lattice spacings d (Å)	Strength	Lattice spacings d (Å)	Strength	Lattice spacings d (Å)	Strength	Lattice spacings d (Å)	Strength
								4.04	16
3.47	Weak							3.42	40
								3.24	40
				2.97	34			2.93	32
2.83	Strong	2.84	Strong	2.88	4	2.70	75	2.83	100
2.36	Weak	2.31	Weak			2.42	45	2.30	32
								2.12	11
2.04	Weak	2.06	Weak	2.06	100			2.02	24
						1.91	45	1.99	24
1.82	Weak							1.87	32
								1.78	16
								1.72	16
1.68	Weak							1.69	16
								1.62	20
								1.56	3
1.47	Weak							1.45	20
								1.40	13
								1.36	13
1.29	Weak							1.29	10

subjected analyze to further in detail.

Therefore, from the pattern of electron diffraction, it is difficult to surely identify the chemical components.

However it is possible that the chemical components were mainly tin sulfide, with which small quantity of ferric sulfide was mixed. It is interesting that there is a larger quantity of sulfide at the bottom of the can-body of the blackened canned salmon, from the estimations of tin and hydrogen sulfide, in comparison with commercial canned salmon. This may be due to the suspending of the tin or ferric sulfide in the liquid. Therefore suspended sulfides may be deposited at the bottom of the can.

The tin sulfide or ferric sulfide may be free from the tin plate of the container at the seaming of the can. In fact, near the seamed part of the container, the exposure of the metal can be found. Therefore, the degree of the blackening of the canned salmon may be affected by the amount of hydrogen sulfide formed from the salmon meat during the processing or storage.

In any case, the blackening of the canned salmon can be prevented by employing

wholly-coated cans, owing to shut out the contact of hydrogen sulfide with metal of tin plate.

IX. RELATION BETWEEN COATED-CANS AND THE SMELL OF CANNED SALMON

As a method of preventing the blackening of various kinds of canned foods, coated-cans have been employed. Recently the coating is to cover the thin layer of electric tin plate on the inner side of the cans in order to prevent rust formation.

When the uncoated-cans (white cans) were employed, even if the unfresh raw salmon is used, of which the freshness had fallen (about 30 *mg%* of V.B.-N content), the decomposed components will combine with the metals of the inner side of the container, and form so-called "the smell of the canned foods", which covers the smell of the decomposed meat. On the contrary, in case of using the wholly-coated cans, there is no exposed metal to combine with the smell of decomposed meat, so the fishy smell assails one's nostrils at the opening of the cans.

Then, what degree of freshness of raw salmon results in the smell which assails to one's nostrils ?

The author has tried to detect the smell, when raw salmon samples, of which the freshness was different, were filled into white cans, coated-cans at top and bottom and wholly-coated cans and processed as usual.

(1) Experimental method

Raw salmon, having various degrees of freshness was packed into various kinds of cans as shown in Table 34, and processed as usual.

Table 34. Samples of test cans

Freshness of raw material (V.B.-N, *mg%*) \ Cans used / Exhausting method	Coated-cans at top and bottom		White cans	Wholly-coated cans	
	by steam-heating	by vacuum-seamer	by vacuum-seamer	by steam-heating	by vacuum-seamer
1[illegible].8 *mg%*	A-1	A′-1	B-1	C-1	C′-1
18.7	A-2	A′-2	B-2	C-2	C′-2
20.1	A-3	A′-3	B-3	C-3	C′-3
21.5	A-4	A′-4	B-4	C-4	C′-4
28.1	A-5	A′-5	B-5	C-5	C′-5
36.4	A-6	A′-6	B-6	C-6	C′-6

After the opening of those cans, the chemical components of the smell were detected by paper chromatography as well as by the method described in the previous experiments.

(2) Expeimental results

Results obtained are shown in Tables 35～40.

Table 35. Smell components in the canned salmon prepared from the fresh material, of which the amount of volatile basic nitrogen was 13.8 *mg*%

Sample cans		A-1	A′-1	B-1	C-1	C′-1
pH		6.0	6.2	6.0	6.0	6.0
V.B.-N after heating (mg%)		33.8	34.4	33.9	35.0	33.9
Juice	Total amount (*cc*)	36.0	38.0	35.0	32.0	37.0
	Water (*cc*)	34.0	32.5	30.0	25.5	30.5
	Oil (*cc*)	2.0	5.5	5.0	5.5	6.5
Water content in meat (%)		70.4	62.9	62.5	65.9	70.9
Amount of adhesion (*g*/can)		3	3	3	3	3
Metals in meat	Total-Fe (*mg*%) (a)	1.7	1.0	2.6	1.1	1.3
	Water-soluble Fe(*mg*%)(b)	0.8	–	0.7	–	–
	$\frac{(b)}{(a)} \times 100$ (%)	47	–	27	–	–
Smell components*	Volatile-bases	a ±	a ±	a ±	a±, b±	a±, b±
	Volatile-acids	k ±	k ±	k ±	k ±	k ±
	Aldehydes	–	–	–	–	–
Organoleptic observation		Meat-color, Smell } good	} good	} good	} good	} good

* Signs of smell components

(1) Volatile bases .... (a) Methylamine, (b) Propylamine, (c) Iso-amylamine, (d) β-phenylethylamine, (e) Agmatine, (f) Cadaverine

(2) Volatile acids .... (k) Formic acid, (l) Acetic acid, (m) Propionic acid, (n) Butyric acid

(3) Aldehydes .... (s) Formaldehyde, (t) Acetaldehyde, (u) Iso-butylaldehyde

(Signs in following tables are the same mean as in this table).

As seen in Tables 35～40, the number of kinds of chemical components (volatile acids or bases, aldehydes) increased with the falling of the freshness of raw salmon used.

The kinds of chemical components of the smell in canned salmon prepared from materials of various freshness are almost the same whatever the kinds of cans used. The amount of ferrous substance, in the meat filled in white cans was larger than that in cans coated at top and bottom or wholly-coated cans. This may be because the chemical components of the meat combined with metals of the container.

When the fresh raw salmon having V.B.-N below 20 *mg*% was used, the smell was not affected by the kinds of cans. But when the degree of freshness of raw salmon fell, of which the amount of V.B.-N was above 20 *mg*%, the fishy smell or decomposed

Table 36. Smell components in the canned salmon prepared from the fresh material, of which the amount of volatile basic nitrogen was 18.7 *mg*%

Sample cans		A-2	A′-2	B-2	C-2	C′-2
pH		6.0	6.2	6.2	6.2	6.0
V.B.-N after heating (*mg*%)		34.2	33.6	34.7	39.8	39.5
Juice	Total amount (*cc*)	25.0	38.0	33.0	29.0	30.0
	Water (*cc*)	24.0	35.0	31.0	28.0	28.5
	Oil (*cc*)	1.0	3.0	2.0	1.0	1.5
Water content in meat (%)		66.4	63.3	65.2	74.6	67.7
Amount of adhesion (*g*/can)		3	3	3	–	3
Metals in meat	Total-Fe (*mg*%) (a)	2.3	2.8	3.0	4.5	1.2
	Water-soluble Fe(*mg*%)(b)	0.3	0.4	0.5	0.5	0.1
	$\frac{(b)}{(a)} \times 100$ (%)	10.7	14.2	16.7	11.1	8.3
Smell components	Volatile-bases	a +	a + c ± d ±	a ± c ± d ±	a + c ± d ±	a + c ± d ±
	Volatile-acids	k ±	k ± l ±	k ±	k ± l ± m ±	k ± l ± m ±
	Aldehydes	–	–	–	–	–
Organoleptic observation		Meat-color, Smell good	good	good	good	good

Table 37. Smell componetns in the canned salmon prepared from pretty fresh material, of which the amount of volatile basic nitrogen was 20.1 *mg*%

Sample cans		A-3	A′-3	B-3	C-3	C′-3
pH		6.2	6.2	6.2	6.2	6.2
V.B.-N after heating (*mg*%)		36.7	36.1	36.7	39.5	38.9
Juice	Total amount (*cc*)	30.0	30.0	31.0	26.0	33.0
	Water (*cc*)	24.0	28.0	25.0	24.5	29.0
	Oil (*cc*)	6.0	2.0	6.0	1.5	4.0
Water content in meat (%)		66.4	63.3	65.2	74.6	67.6
Amount of adhesion (*g*/can)		–	–	3	3	3
Metals in meat	Total-Fe (*mg*%) (a)	2.6	2.8	4.7	–	–
	Water-soluble Fe(*mg*%)(b)	0.2	0.3	0.8	1.0	0.4
	$\frac{(b)}{(a)} \times 100$ (%)	7.7	10.7	17.0	–	–
Smell components	Volatile-bases	a + b + e ±	a + e ±	a + c ± e ±	a + b + e +	a + d + e +
	Volatile-acids	k ±	k ± l +	k ±	k + l + m +	k + l +
	Aldehydes	s ± t ±	s ± t ±	s ± t ±	s + t ±	s ± t ±
Organoleptic observation		Good appearance, Slight "smell of canned foods"	Same as left	Same as left	Slight fishy smell	Same as left

Table 38. Smell components in the canned salmon prepared from pretty unfresh material, of which the amount of volatile basic nitrogen was 21.5 *mg*%

Sample cans		A-4	A′-4	B-4	C-4	C′-4
pH		6.2	6.2	6.2	6.2	6.2
V.B.-N after heating (*mg*%)		38.9	33.0	35.3	40.3	37.7
Juice	Total amount (*cc*)	24.0	29.0	29.0	25.0	32.0
	Water (*cc*)	22.5	27.5	27.0	23.5	30.0
	Oil (*cc*)	1.5	1.5	2.0	1.5	2.0
Water content in meat (%)		66.1	67.5	72.3	69.8	72.1
Amount of adhesion (*g*/can)		3	3	4	–	–
Metals in meat	Total-Fe (*mg*%) (a)	6.2	3.7	7.1	2.4	3.4
	Water-soluble Fe(*mg*%)(b)	1.9	3.2	2.6	1.6	1.9
	$\frac{(b)}{(a)} \times 100$ (%)	30.6	86.6	36.6	66.7	50.9
Smell components	Volatile-bases	a ±, b ± c +, e +	a ±, c + e +	a ±, c + e +	a ±, d + e +, f +	d +, e + f +
	Volatile-acids	k + l +	k + l +	k + l +	k +, l + m +	k +, l + m ±
	Aldehydes	s + t +	s + t +	s + t ±	s ± t +	s +, t + u +
Organoleptic observation		Meat color was slight brownish, Slight "smell of canned foods"	Same as left	Same as left	Meat was slight brownish, Slight fishy smell	Same as left

Table 39. Smell components in the canned salmon prepared from unfresh material, of which the amount of volatile basic nitrogen was 28.1 *mg*%

Sample cans		A-5	A′-5	B-5	C-5	C′-5
pH		6.0	6.0	6.0	6.0	6.0
V.B.-N after heating (*mg*%)		38.1	40.3	34.7	39.2	40.8
Juice	Total amount (*cc*)	30.0	30.0	25.0	25.0	28.0
	Water (*cc*)	28.5	28.5	23.0	23.0	26.5
	Oil (*cc*)	1.8	1.5	2.0	2.0	1.5
Water content in meat (%)		65.9	69.0	63.3	68.4	72.4
Amount of adhesion (*g*/can)		–	–	–	–	–
Metals in meat	Total-Fe (*mg*%) (a)	6.2	2.4	8.0	6.2	2.8
	Water-soluble Fe(*mg*%)(b)	1.3	1.5	7.1	3.7	1.3
	$\frac{(b)}{(a)} \times 100$ (%)	20.9	62.5	88.8	59.7	46.5
Smell components	Volatile-bases	b + c + d ±	c + e + f ±	d + e + f ±	d + e + f +	d + e + f +
	Volatile-acids	k +, l + m ±, n ±	k +, l + m ±, n +	k +, l + m +, n ±	k +, l + m +, n ±	k +, l + m +, n ±
	Aldehydes	s + t + u +	s + t + u +	s + t + u +	s + t + u +	s + t + u +
Organoleptic observation		Meat was brownish, Curd fromation was remarkable, Slight "smell of canned foods"	Same as left	Same as left	Meat was brownish, Curd was remarkable, Strong fishy smell	Same as left

Table 40. Smell components in the canned salmon prepared from unfresh material, of which the amount of volatile basic nitrogen was 36.4 *mg*%

Sample cans		A-6	A′-6	B-6	C-6	C′-6
pH		6.0	6.2	6.2	6.2	6.2
V.B.-N after heating (*mg*%)		59.9	67.2	54.9	53.5	59.9
Juice	Total amount (*cc*)	35.0	31.0	30.0	33.0	31.0
	Water (*cc*)	30.0	25.0	27.0	29.0	29.5
	Oil (*cc*)	5.0	6.0	3.0	4.0	1.5
Water content in meat (%)		63.7	62.2	65.1	67.1	68.2
Amount of adhesion (*g*/can)		3	5	4	2	8
Metals in meat	Total-Fe (*mg*%) (a)	6.2	5.2	8.1	3.4	3.4
	Water-soluble Fe(*mg*%)(b)	4.3	3.0	6.6	2.3	–
	$\frac{(b)}{(a)} \times 100$ (%)	69.4	57.7	81.0	67.7	–
Smell components	Volatile-bases	b + c + e +	c + e + f +	c + e + f +	d + e + f +	d + e + f +
	Volatile-acids	k + l + m + n +	k + l + m + n +	k + l + m + n +	k + l + m + n +	k + l + m + n +
	Aldehydes	s + t + u +	s + t + u +	s + t + u +	s + t + u +	s + t + u +
Organoleptic observation		Decomposed smell, Meat softened	Decomposed smell	Same as left	Same as left	Same as left

smell assailed one's nostrils from material in cans coated at top and bottom or from wholly-coated cans. Whereas, in white cans "the smell of canned foods" was clearly detected, but the smell liberated from the decomposed meat was inconsiderable. If coated-cans were employed, therefore, the freshness of raw salmon should be below 20 *mg*%, which has been offered by the present author as "the limit of the freshness of raw material for the canning".

SUMMARY

In this paper, the author has discussed the decomposition of canned salmon (liquefied and swelled types), and has clarified the cause of the decomposition. According to the observations, the cans were understerilized. This may be due to the fact that even if unfresh raw salmon was prepared for the canning, the processing temperature and time used were the same as in case of fresh raw material. Here the author has made a scale which shows the adequate processing time corresponding to the various degrees of freshness of raw salmon used. By this scale, the freshness of raw salmon can be estimated, when the leaving time between catching and processing

and storing temperature of the raw materials are already known. Next, when the degree of freshness is known, the adequate processing time will be determined at the certain definite processing temperature.

The blackening of the canned salmon is affected by the freshness of the raw salmon, and the smell of the canned salmon packed in coated-cans is also affected by the freshness.

In this paper, the smell of the canned salmon prepared from frozen salmon was studied. This smell was clarified to be formed from the oxidation of raw salmon fat and oil during the freezing storage. So, frozen salmon should be prepared for canning within 50 days of storage. In order to prevent the oxidation of oil, "Sustane 1-F" should be applied to raw salmon and the salmon should then be frozen.

In the technical problems, the freshness of the raw salmon plays the main part. Therefore, in salmon canning, the raw material should be always fresh, and the treatment should be rapidly performed.

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